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# PATENT COOPERATION TREATY

## PCT

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### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>47134</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/FI98/01004</b>	International filing date (day/month/year) <b>21/12/1998</b>	Priority date (day/month/year) <b>23/12/1997</b>
International Patent Classification (IPC) or national classification and IPC <b>C07F3/00</b>		
Applicant <b>BOREALIS A/S et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 7 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand <b>13/07/1999</b>	Date of completion of this report <b>24.01.00</b>
Name and mailing address of the international preliminary examining authority:  <b>European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465</b>	Authorized officer <b>Stroeter, T</b> Telephone No. +49 89 2399 8088 

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/FI98/01004

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1,6-28	as originally filed			
2-5	as received on	29/12/1999	with letter of	27/12/1999

### Claims, No.:

1-32	as received on	29/12/1999	with letter of	27/12/1999
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### Drawings, sheets:

2/5-5/5	as originally filed			
1/5	as received on	29/12/1999	with letter of	27/12/1999

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/FI98/01004

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1-32
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-32
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/FI98/01004

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1     Subject-matter of the Independent Claims**

The present application refers to complexes comprising a magnesium dihalide and an oxygen-containing electron donor and claims said products (independent claim 1), their preparation (independent claim 10) and use (independent claim 29).

**2     Prior Art Documents**

Reference is made to the following documents. The given numbering will be adhered to in the rest of the procedure:

D1: EP-A-0 297 076 (LITHIUM CORPORATION OF AMERICA) 28 December 1988

D1 discloses adducts of magnesium dihalides with alcohols as electron donors for the use as starting materials for the preparation of olefin polymerisation catalysts.

D2: US-A-4 727 051 (BREEN, M.J. ET AL.) 23 February 1988

D2 refers to non-soluble alkoxymagnesium halides, which are not compounds of higher order and as such not to be regarded as complexes. Therefore the content of D2 was not regarded as relevant for the examination according the Articles 33(2) and 33(3) PCT.

3 Novelty (Article 33(2) PCT)

As could be stated by comparison of the present application with the documents cited in the European Search Report, filed claims 1 to 32 fulfil the requirements of Article 33(2) PCT, because in none of the prior art documents D1 or D2 similar compositions of magnesium-containing complexes could be found and as such the preparation of those complexes and their use for the preparation of a polymer catalyst is new, too.

4 Inventive Step (Article 33(3) PCT)

In order to examine the content of the present application with respect to Article 33(3) PCT, Document D1 was considered to represent the **most relevant state of the art**.

The **technical effect** as provided by the compounds of claim 1 of the present application over closest prior art document D1 is that said compounds, when used for preparing olefin polymerisation catalysts, do not react with titanium halide to give unwanted by-products.

Therefore the **technical problem** to be solved by the present application is how to provide a complex consisting of a magnesium halide and an electron donor, the latter not reacting with titanium halide.

The **technical solution** to achieve the results as mentioned above is to be seen in the compounds of formula (I) as claimed in claim 1.

It is assumed that a man skilled in the art would not be able to derive the subject-matter of the present invention from the technical content of D1 in an obvious manner. **No indication** is given in the other prior art documents that donors as the ester and ether compounds of the present application could be combined with magnesium halides *before* the reaction with the titanium halide.

The subject-matter of claim 1 is at present considered new and inventive in view of D1 and the prior art. Related independent process and use claims 10 resp. 29, are also regarded to be inventive according to Article 33(3) PCT. The same holds for all present dependent claims.

5 Industrial applicability (Article 33(4) PCT)

The subject-matter of the present set of claims 1 to 32 is in accordance with the requirements of Article 33(4) PCT.

6 Summary

**Thus, the whole set of claims 1 to 32 of the present application is regarded as new, inventive and industrial applicable according to Articles 33(2), 33(3) and 33(4) PCT.**

**Re Item VIII**

**Certain observations on the international application**

1 Clarity of the Claims (Article 6 PCT)

- 1.1 Amended claims 21 and 23 lack support by the description because the amendments were not introduced in the equivalent section in the description on page 6, line 21.
- 1.2 Amended claim 24 still lacks clarity and probably should read: "...complex of a magnesium dihalide and **an alcohol** is a complex of magnesium dichloride and an alcohol..." according to the teaching of the description on page 7, line 8.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/FI98/01004

1.3 Amended claim 32 also still lacks clarity for the following reasons:

a) The description teaches that the wavenumber of the uncoordinated CO-double bond is  $1729\text{ cm}^{-1}$  and therefore it is not clear why claim 32 reads "... a main absorption peak at  $1729\text{ cm}^{-1}$  for the C=O...Mg that...".

b) The statement "...has shifted...to the right..." must be linked with a certain action (storage overnight) according to the content of the description on page 11, third paragraph. Furthermore, as a consequence of the present wording it is not clear whether the value of  $1729\text{ cm}^{-1}$  is the consequence or the starting point for said shift.

1.4 "Wavelength" as on page 11, line 2 of the present description is an incorrect term in the given context.

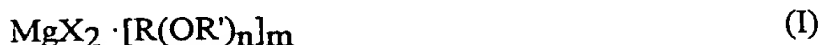




Typical examples of solvents that are able to form complexes with  $\text{MgCl}_2$  are alcohols and water. These compounds have, however, a reactive hydrogen in the hydroxyl group of their molecule which easily reacts with other compounds such as titaniumhalides. Examples of less reactive solvents are the organic esters. They are less reactive towards other components but at the same time they do not have the ability to break up the strongly co-ordinated  $\text{MgCl}_2$  molecules. In view of the teaching of the prior art, it seems impossible to achieve amorphous  $\text{MgCl}_2$  without harmful side reactions.

10 The purpose of the invention is therefore to produce amorphous magnesium dihalide *in situ* without wasting titanium halide or producing harmful waste products. The invention also aims at a stoichiometric route for the preparation of Ziegler-Natta catalyst components and their intermediates. By a stoichiometric route, new catalyst components for the production of tailor-made olefin polymers can be produced.

15 The purposes of the invention has been achieved by means of a complex comprising a magnesium dihalide and an electron donor, which is characterized in that it is a complex of the magnesium dihalide and the electron donor and has the formula (I):



20 wherein  $\text{MgX}_2$  is the magnesium dihalide and  $\text{R}(\text{OR}')_n$  is the electron donor, X is a halogen, R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, R' is a  $\text{C}_1\text{-C}_{20}$  alkyl group or a  $\text{C}_7\text{-C}_{27}$  aralkyl group, n is a number from 1 to 6 and m is defined as a number  $0.5 \leq m \leq 2.0$ . By "n-valent acyclic group" is meant a group having n acyl moieties.

25 Formula (I) is an empirical or semiempirical formula, i.e. m expresses the ratio between the the electron donor  $\text{R}(\text{OR}')_n$  and magnesium dihalide  $\text{MgX}_2$ . The structural formula may have several molecules of  $\text{MgX}_2$  and several same or different molecules of  $\text{R}(\text{OR}')_n$ , such as in the complex  $(\text{MgX}_2)_a \cdot [\text{R}(\text{OR}')_n]_b$  wherein  $b:a = m$ . See e.g. formula (III) below. The claimed complex may be a statistical one, being a mixture of complexes having the average formula (I), or a specific one, 30 essentially all the molecules of which having the same formula (I).

In the magnesium dihalide molecular component  $\text{MgX}_2$  of the complex, X is preferably selected from Cl, Br and I, and is most preferably Cl. The most preferred complex according to the invention is thus a magnesium dichloride complex.

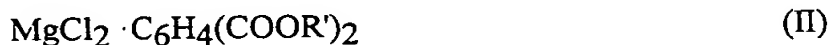
In the electron donor molecular component  $R(OR')_n$  of the complex, R is preferably an n-valent  $C_2-C_{22}$  acyclic group, more preferably an n-valent aromatic  $C_7-C_{22}$  acyclic group, most preferably phthaloyl. R' is preferably a  $C_6-C_{16}$  alkyl, most preferably a  $C_6-C_{12}$  alkyl like undecyl or 2-ethyl-1-hexyl. It means that the phthalate preferably should be an ester of phthalic acid and a longer-chained alcohol. n is preferably about 1 to about 4, preferably about 2, meaning preference for a phthalic acid diester (phthalic acid is dibasic). By "acyclic group" is meant the general name for organic acid groups, which form the remainder of carboxylic acids after removing the hydroxyl group.

Thus, the most preferred complex is that of one of the most efficient magnesium compounds and one of the most efficient internal electron donors in the art of Ziegler-Natta catalysts, namely magnesium dichloride and a phthalic acid ester.

In the claimed complex as a whole, m depicts the average ratio between the electron donor molecular component  $R(OR')_n$  and the magnesium dihalide molecular component  $MgX_2$ . m is preferably about 0.67 to about 1.0, most preferably about 0.67 or about 1.0. See below, structural formulas (II) and (III).

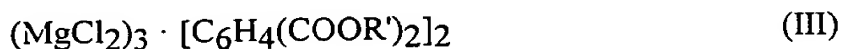
The complex according to the invention is preferably a magnesium dichloride phthalic acid ester complex having the formula  $MgCl_2 \cdot [C_6H_4(COOR')_2]_m$ , wherein R' is the same as above and m is from 0.5 to 2.0, most preferably from 0.6 to 1.8.

According to one embodiment of the complex of the invention, the complex is preferably a magnesium dichloride phthalic acid ester complex having the structural formula (II):



wherein R' is the same as above.

According to another embodiment of the complex of the invention, the complex is a magnesium dichloride phthalic acid ester complex having the structural formula (III):



wherein R' is the same as above.

Typically, the claimed complex has an X-ray diffraction pattern (measured by a Siemens D500 instrument equipped with a Cu anode and a graphite monochromator in the reflected beam and using an effect of 40 kV and 35 mA and a  $\text{CuK}\alpha$  radiation wavelength of 1.541 Å), showing a dominant peak at  $4.5^\circ 2\Theta$ .

- 5 The invention also relates to a process for the preparation of a complex comprising a magnesium dihalide and an electron donor.

Characteristic of the claimed process is that a magnesium compound (a) containing an alkoxy moiety, which magnesium compound is selected from the group consisting of a complex of a magnesium dihalide and a magnesium dialkoxide, a  
10 complex of a magnesium dihalide and an alcohol, and a non-complex magnesium dialkoxide, is reacted with a halogen compound (b), which is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety.

According to the most important aspect of the invention, the process is a part of a novel stoichiometric preparation process leading to novel catalyst components for  
15 olefin polymerization.

The halogen compound (b) is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety. This does not only mean that the halogen compound is a reagent leading to the electron donor, but also that it is a structural precursor thereof. Compare e.g. an alkyl halide with the corresponding dialkyl ether  
20 or an organic acid halide with the corresponding organic acid ester.

The halogen compound (b) preferably has the formula (IV):



wherein R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, X is a halogen and n is 1 to 6. In the  
25 formula, R is preferably an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, more preferably an n-valent aromatic  $\text{C}_7\text{-C}_{24}$  acyclic group, most preferably phthaloyl. X is preferably selected from Cl, Br and I, and is preferably Cl. n is preferably 1 to 4, most preferably about 2.

According to a preferred embodiment of the process of the invention, said halogen  
30 compound (b) is an organic acid halide, preferably phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene. When one considers that the most preferred internal electron donor molecule of the claimed complex is a phthalic acid ester, the

complexed ester molecule is simply formed by replacing the chlorines of the phthalic acid dichloride with alkoxy groups.

According to a first alternative embodiment of the process of the invention, said magnesium compound (a) containing an alkoxy moiety is a magnesium dichloride-magnesium dialkoxide complex of the formula (V):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group, and p is 1 to 6, preferably about 2. Formula (V) is empirical or semiempirical, meaning that the complex's molecular clusters can consist of several MgCl<sub>2</sub> molecules and several Mg(OR')<sub>2</sub> molecules, corresponding to the formula (MgCl<sub>2</sub>)<sub>c</sub>[Mg(OR')<sub>2</sub>]<sub>d</sub> wherein d:c = p. In the process of the invention, said magnesium dichloride-magnesium dialkoxide complex is reacted with the above halogen compound so that the halogen compound (b) has its halogen(s) replaced by the alkoxide(s) of the complex and forms an electron donor, whereby the complex of magnesium dichloride and the electron donor is formed.

Preferably, said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-dimagnesium dialkoxide complex of the structural formula (VI):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

Said magnesium dichloride-magnesium dialkoxide complex is preferably prepared by reacting magnesium dichloride and an alcohol into an intermediate which is a magnesium dichloride-alcohol complex MgCl<sub>2</sub> · (R'OH)<sub>2p</sub> wherein R' is the same as above, and reacting the magnesium dichloride alcohol complex with p mol of a magnesium dialkyl MgR''<sub>2</sub>, wherein R'' is a hydrocarbyl group having 1 to 20 carbon atoms. If R'' is a hydrocarbyl group having 1 to 5 carbon atoms, a volatile alkane R''H byproduct is thereby formed and easily removed by evaporation. In the synthesis, the molar ratio MgCl<sub>2</sub>:R'OH is preferably between 1:1 and 1:8, most preferably between 1:2 and 1:5. The molar ratio MgCl<sub>2</sub> · (R'OH)<sub>2p</sub>:MgR''<sub>2</sub> is preferably between 1:1 and 1:4, most preferably about 1:2.

## Claims

1. A complex comprising a magnesium dihalide and an electron donor, characterized in that it is a complex of the magnesium dihalide and the electron donor and has the following formula (I) expressing the molar ratio between the magnesium dihalide and the electron donor:



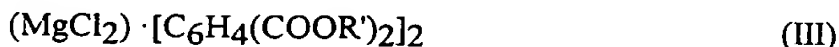
wherein  $\text{MgX}_2$  is the magnesium dihalide and  $\text{R}(\text{OR}')_n$  is the electron donor, X is a halogen, R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, R' is a  $\text{C}_1\text{-C}_{20}$  alkyl group or a  $\text{C}_7\text{-C}_{27}$  aralkyl group, n is a number from 1 to 6 and m is defined as a number  $0.5 \leq m \leq 2.0$ .

2. The complex according to Claim 1, characterized in that X is selected from Cl, Br and I, and is preferably Cl.
3. The complex according to Claim 1 or 2, characterized in that R is an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, preferably an n-valent aromatic  $\text{C}_7\text{-C}_{22}$  acyclic group, most preferably phthaloyl.
4. The complex according to Claim 1, 2 or 3, characterized in that R' is a  $\text{C}_6\text{-C}_{16}$  alkyl group, preferably a  $\text{C}_6\text{-C}_{12}$  alkyl group like undecyl or 2-ethyl-1-hexyl.
5. The complex according to any preceding claim, characterized in that n is about 1 to about 4, preferably about 2.0.
6. The complex according to any preceding claim, characterized in that m is about 0.67 to about 1.0.
7. The complex according to any preceding claim, characterized in that it is a magnesium dichloride phthalic acid ester complex having the formula (II):



wherein R' is the same as above.

8. The complex according to one of Claims 1 to 5, characterized in that it is a magnesium dichloride phthalic acid ester complex having the formula (III):



wherein R' is the same as above.

9. The complex according to any preceding claim, characterized in that it has an X-ray diffraction pattern showing a dominant peak at  $4.5^{\circ}2\Theta$ .

10. Process for the preparation of a complex according to any preceding claim comprising a magnesium dihalide and an electron donor, characterized by reacting a magnesium compound (a) containing an alkoxy moiety, which magnesium compound is selected from the group consisting of a complex of a magnesium dihalide and a magnesium dialkoxide, a complex of a magnesium dihalide and an alcohol, and a non-complex magnesium dialkoxide, with a halogen compound (b), which is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety.

11. Process according to Claim 10, characterized in that said halogen compound (b) has the formula (IV):



wherein R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, X is a halogen and n is 1 to 6.

12. The complex according to Claim 11, characterized in that R is an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, preferably an n-valent aromatic  $\text{C}_7\text{-C}_{24}$  acyclic group, most preferably phthaloyl.

13. Process according to Claim 11 or 12, characterized in that X is selected from Cl, Br and I, and is preferably Cl.

14. Process according to Claim 11, 12 or 13, characterized in that n is 1 to 4, preferably about 2.

15. Process according to any of Claims 11 to 14, characterized in that said halogen compound is an organic acid halide, preferably phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene.

16. Process according to any of Claims 10 to 15, characterized in that said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-magnesium dialkoxide complex of the formula (V):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group, and p is 1 to 6, preferably about 2.

17. Process according to Claim 16, characterized in that said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-dimagnesium dialkoxide complex of the formula (VI):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

18. Process according to Claim 16, characterized in that said magnesium dichloride magnesium dialkoxide complex is prepared by reacting magnesium dichloride with an alcohol into an intermediate which is a magnesium dichloride alcohol complex  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_{2p}$ , wherein R' is the same as above, and reacting the magnesium dichloride alcohol complex with p mol of a magnesium dialkyl  $\text{MgR}''_2$ , wherein R'' is a hydrocarbonyl group having 1 to 20 carbon atoms.

19. Process according to Claim 18, characterized in that, independently, the molar ratio  $\text{MgCl}_2:\text{R}'\text{OH}$  is between 1:1 and 1:8, preferably between 1:2 and 1:5, the molar ratio  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_{2p}:\text{MgR}''_2$  is between 1:1 and 1:4, preferably about 1:2, the temperature is between 80 °C and 160 °C, and the reaction time is about 2 h to about 8 h.

20. Process according to Claim 15 and 17, characterized in that said magnesium compound (a) which is said magnesium dichloride-dimagnesium dialkoxide complex  $\text{MgCl}_2 \cdot [\text{Mg}(\text{OR}')_2]_2$ , wherein R' is a C<sub>6</sub>-C<sub>16</sub> alkyl group, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene.

21. Process according to any of Claims 10 to 15, characterized in that said non-complex magnesium dialkoxide has the formula (VIII):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> aralkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

22. Process according to Claim 21, characterized in that said non-complex magnesium dialkoxide is prepared by reacting a magnesium dialkyl, preferably a

magnesium dialkyl of the formula  $\text{MgR}''_2$ , wherein  $\text{R}''$  is a hydrocarbyl group having 1 to 20 carbon atoms, and an alcohol, preferably an alcohol of the formula  $\text{R}'\text{OH}$  wherein  $\text{R}'$  is the same as above.

23. Process according to Claim 15 and 21, characterized in that said magnesium compound (a) which is said non-complex magnesium dialkoxide has the formula  $\text{Mg}(\text{OR}')_2$ , wherein  $\text{R}'$  is a  $\text{C}_1\text{-C}_{20}$  aralkyl or a  $\text{C}_7\text{-C}_{27}$  aralkyl, preferably a  $\text{C}_6\text{-C}_{16}$  alkyl, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene.

24. Process according to any of Claims 10 to 15, characterized in that said complex of a magnesium dihalide and a magnesium dialkoxide is a complex of a magnesium dihalide and an alcohol having the formula (VII):



wherein  $\text{R}'$  is a  $\text{C}_1\text{-C}_{20}$  alkyl group or a  $\text{C}_7\text{-C}_{27}$  aralkyl group, preferably a  $\text{C}_6\text{-C}_{16}$  alkyl group, and  $q$  is from 1 to 6.

25. Process according to Claim 24, characterized in that said complex of a magnesium dihalide and an alcohol is prepared by reacting magnesium dichloride  $\text{MgCl}_2$  and alcohol  $\text{R}'\text{OH}$ , wherein  $\text{R}'$  is the same as above.

26. Process according to Claim 24 or 25, characterized in that the reaction temperature is kept between  $10^\circ\text{C}$  and  $100^\circ\text{C}$ , and the reaction time is about from 10 to about 90 min.

27. Process according to Claim 15 and 24, characterized in that said magnesium compound (a) which is said complex of a magnesium dihalide and an alcohol having the formula  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_q$ , wherein  $\text{R}'$  is a  $\text{C}_1\text{-C}_{20}$  alkyl or a  $\text{C}_7\text{-C}_{27}$  aralkyl, preferably a  $\text{C}_6\text{-C}_{16}$  alkyl, and  $q$  is from 1 to 6, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene.

28. Process according to one of Claims 10 to 27, characterized in that said magnesium compound (a) and said halogen compound (b) are reacted essentially stoichiometrically.

29. Use of a complex according to one of Claims 1 to 9 or a complex prepared according to one of Claims 10 to 28 for the preparation of a polymerization catalyst component containing magnesium, transition metal, halogen and electron donor.



30. Use according to Claim 29, characterized in that said complex is reacted with a titanium halide (c).

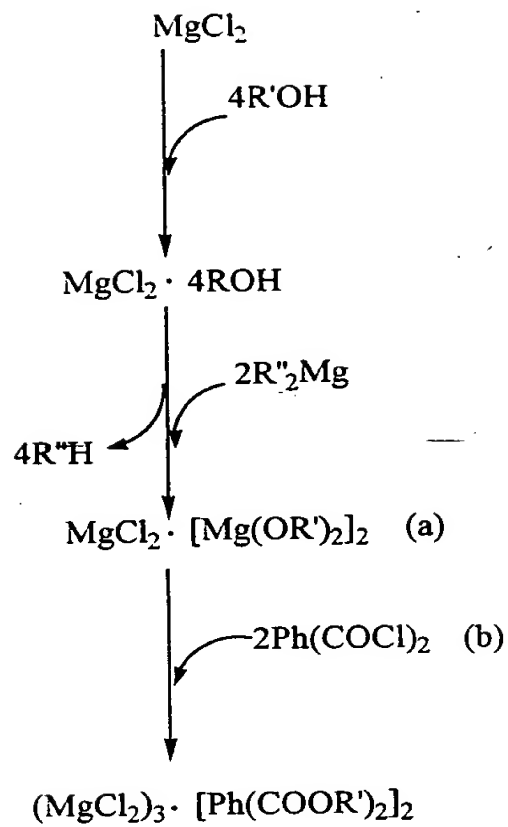
31. Use according to Claim 30, characterized in that said titanium halide (c) has the formula (IX):



wherein R''' is a C<sub>1</sub>-C<sub>10</sub> alkyl group or a C<sub>7</sub>-C<sub>16</sub> aralkyl group, X is a halogen and p is 0 to 3, and preferably is a titanium tetrahalide TiX<sub>4</sub>, wherein X is the same as above, most preferably titanium tetrachloride TiCl<sub>4</sub>.

10 32. A complex according to one of claims 1 to 9, characterized in that it shows an IR spectra with an absorption peak for the C=O...Mg that has shifted 5 to 15 cm<sup>-1</sup>, preferably 10 cm<sup>-1</sup> to the right, and preferably also shows three shoulders.

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**Figure 1** Example of first alternative embodiment

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<b>(21) International Application Number:</b> PCT/FI98/01004 <b>(22) International Filing Date:</b> 21 December 1998 (21.12.98) <b>(30) Priority Data:</b> 974622 23 December 1997 (23.12.97) FI 974623 23 December 1997 (23.12.97) FI <b>(71) Applicant (for all designated States except US):</b> BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GAROFF, Thomas [FI/FI]; Kirkkosalmentie 6 A 5, FIN-00840 Helsinki (FI). LEINONEN, Timo [FI/FI]; Massatie 8, FIN-06750 Tolkkinen (FI). ALA-HUIKKU, Sirpa [FI/FI]; Korvatunturintie 5 B, FIN-00970 Helsinki (FI). <b>(74) Agent:</b> BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SOLUBLE MAGNESIUM DIHALIDE COMPLEX, PREPARATION AND USE  <b>(57) Abstract</b> <p>The invention relates to a complex comprising a magnesium dihalide and an electron donor. It is a complex of the magnesium dihalide and the electron donor and has the formula (I): <math>MgX_2 \cdot [R(OR')_n]_m</math> wherein <math>MgX_2</math> is the magnesium dihalide and <math>R(OR')_n</math> is the electron donor, X is a halogen, R is an n-valent <math>C_1-C_{20}</math> aliphatic group, an n-valent <math>C_7-C_{27}</math> araliphatic group or an n-valent <math>C_2-C_{22}</math> acyclic group, R' is a <math>C_1-C_{20}</math> alkyl group or a <math>C_7-C_{27}</math> aralkyl group, n is a number from 1 to 6 and m is defined as a number <math>0.5 \leq m \leq 2.0</math>. The invention also relates to the preparation process of such a complex, as well as the use thereof for the preparation of olefin polymerization catalyst components.</p>		

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## SOLUBLE MAGNESIUM DIHALIDE COMPLEX, PREPARATION AND USE

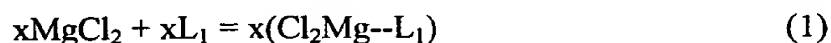
The invention relates to a soluble complex comprising a magnesium dihalide and an electron donor. The invention also relates to a process for the preparation of such a complex, as well as the use of such a complex for the preparation of a polymerization catalyst component containing magnesium, transition metal, halogen and electron donor.

A complex is, according to Römpps Chemie-Lexikon, 7. Edition, Franckh'sche Verlagshandlung, W. Keller & Co., Stuttgart, 1973, page 1831, "a derived name of compounds of higher order, which originates from the combination of molecules, - unlike compounds of first order, in the creation of which atoms participate".

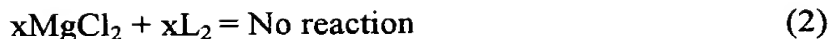
Generally, so called Ziegler-Natta catalyst components have been prepared by reacting a magnesium dihalide-alcohol complex compound or a magnesium alkoxide non-complex compound with a titanium halide and an electron donor which usually is a phthalic acid ester. It is necessary that the magnesium dihalide is amorphous for the catalyst component to be active. Amorphous magnesium dihalide is thus produced *in situ*.

When reacting the titanium halide with the magnesium dihalide-alcohol complex compound or the magnesium alkoxide non-complex compound, the titanium halide form titanium alkoxy trihalide, which is a harmful waste product. Both reactions have the disadvantage that the titanium halide is wasted for other purposes than the direct provision of catalytically active sites, such as chlorination of the magnesium reactant and washing away of the harmful titanium alkoxy trihalide.

In the production of amorphous magnesium dihalide, such as  $\text{MgCl}_2$  strong polar ligand groups ( $\text{L}_1$ ) are needed in order to break up the strong electrostatic crystalline bonds between the  $\text{MgCl}_2$  molecules according to reaction (1):



In practice, polar solvents are needed to carry out reaction (1). In several cases these polar solvents are reactive towards other parts of the catalyst component, and thus have to be replaced by less polar solvents ( $\text{L}_2$ ). These less polar solvents are, however, often unable to react and co-ordinate with  $\text{MgCl}_2$  due to the strong intermolecular forces in the  $\text{MgCl}_2$  structure (2):



Typical examples of solvents that are able to form complexes with  $\text{MgCl}_2$  are alcohols and water. These compounds have, however, a reactive hydrogen in the hydroxyl group of their molecule which easily reacts with other compounds such as titaniumhalides. Examples of less reactive solvents are the organic esters. They are less reactive towards other components but at the same time they do not have the ability to break up the strongly co-ordinated  $\text{MgCl}_2$  molecules. In view of the teaching of the prior art, it seems impossible to achieve amorphous  $\text{MgCl}_2$  without harmful side reactions.

10 The purpose of the invention is therefore to produce amorphous magnesium dihalide *in situ* without wasting titanium halide or producing harmful waste products. The invention also aims at a stoichiometric route for the preparation of Ziegler-Natta catalyst components and their intermediates. By a stoichiometric route, new catalyst components for the production of tailor-made olefin polymers can be produced.

15 The purposes of the invention has been achieved by means of a complex comprising a magnesium dihalide and an electron donor, which is characterized in that it is a complex of the magnesium dihalide and the electron donor and has the formula (I):



wherein  $\text{MgX}_2$  is the magnesium dihalide and  $\text{R}(\text{OR}')_n$  is the electron donor, X is a halogen, R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, R' is a  $\text{C}_1\text{-C}_{20}$  alkyl group or a  $\text{C}_7\text{-C}_{27}$  aralkyl group, n is a number from 1 to 6 and m is defined as a number  $0.5 \leq m \leq 2.0$ . By "n-valent acyclic group" is meant a group having n acyl moieties.

Formula (I) is an empirical or semiempirical formula, i.e. m expresses the ratio between the the electron donor  $\text{R}(\text{OR}')_n$  and magnesium dihalide  $\text{MgX}_2$ . The structural formula may have several molecules of  $\text{MgX}_2$  and several same or different molecules of  $\text{R}(\text{OR}')_n$ , such as in the complex  $(\text{MgX}_2)_a \cdot [\text{R}(\text{OR}')_n]_b$  wherein  $b:a = m$ . See e.g. formula (III) below. The claimed complex may be a statistical one, being a mixture of complexes having the average formula (I), or a specific one, essentially all the molecules of which having the same formula (I).

In the magnesium dihalide molecular component  $\text{MgX}_2$  of the complex, X is preferably selected from Cl, Br and I, and is most preferably Cl. The most preferred complex according to the invention is thus a magnesium dichloride complex.

In the electron donor molecular component  $R(OR')_n$  of the complex, R is preferably an n-valent  $C_2$ - $C_{22}$  acyclic group, more preferably an n-valent aromatic  $C_7$ - $C_{22}$  acyclic group, most preferably phthaloyl. R' is preferably a  $C_6$ - $C_{16}$  alkyl, most preferably a  $C_6$ - $C_{12}$  alkyl like undecyl or 2-ethyl-1-hexyl. It means that the phthalate preferably should be an ester of phthalic acid and a longer-chained alcohol. n is preferably about 1 to about 4, preferably about 2, meaning preference for a phthalic acid diester (phthalic acid is dibasic). By "acyclic group" is meant the general name for organic acid groups, which form the remainder of carboxylic acids after removing the hydroxyl group.

Thus, the most preferred complex is that of one of the most efficient magnesium compounds and one of the most efficient internal electron donors in the art of Ziegler-Natta catalysts, namely magnesium dichloride and a phthalic acid ester.

In the claimed complex as a whole, m depicts the average ratio between the electron donor molecular component  $R(OR')_n$  and the magnesium dihalide molecular component  $MgX_2$ . m is preferably about 0.67 to about 1.0, most preferably about 0.67 or about 1.0. See below, structural formulas (II) and (III).

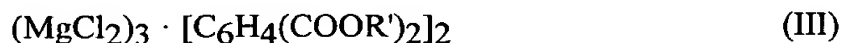
The complex according to the invention is preferably a magnesium dichloride phthalic acid ester complex having the formula  $MgCl_2 \cdot [C_6H_4(COOR')_2]_m$ , wherein R' is the same as above and m is from 0.5 to 2.0, most preferably from 0.6 to 1.8.

According to one embodiment of the complex of the invention, the complex is preferably a magnesium dichloride phthalic acid ester complex having the structural formula (II):



wherein R' is the same as above.

According to another embodiment of the complex of the invention, the complex is a magnesium dichloride phthalic acid ester complex having the structural formula (III):



wherein R' is the same as above.

Typically, the claimed complex has an X-ray diffraction pattern (measured by a Siemens D500 instrument equipped with a Cu anode and a graphite monochromator in the reflected beam and using an effect of 40 kV and 35 mA and a  $\text{CuK}\alpha$  radiation wavelength of 1.541 Å), showing a dominant peak at  $4.5^\circ 2\Theta$ .

- 5 The invention also relates to a process for the preparation of a complex comprising a magnesium dihalide and an electron donor.

Characteristic of the claimed process is that a magnesium compound (a) containing an alkoxy moiety, which magnesium compound is selected from the group consisting of a complex of a magnesium dihalide and a magnesium dialkoxide, a  
10 complex of a magnesium dihalide and an alcohol, and a non-complex magnesium dialkoxide, is reacted with a halogen compound (b), which is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety.

According to the most important aspect of the invention, the process is a part of a novel stoichiometric preparation process leading to novel catalyst components for  
15 olefin polymerization.

The halogen compound (b) is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety. This does not only mean that the halogen compound is a reagent leading to the electron donor, but also that it is a structural precursor thereof. Compare e.g. an alkyl halide with the corresponding dialkyl ether  
20 or an organic acid halide with the corresponding organic acid ester.

The halogen compound (b) preferably has the formula (IV):



wherein R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, X is a halogen and n is 1 to 6. In the  
25 formula, R is preferably an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, more preferably an n-valent aromatic  $\text{C}_7\text{-C}_{24}$  acyclic group, most preferably phthaloyl. X is preferably selected from Cl, Br and I, and is preferably Cl. n is preferably 1 to 4, most preferably about 2.

According to a preferred embodiment of the process of the invention, said halogen  
30 compound (b) is an organic acid halide, preferably phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene. When one considers that the most preferred internal electron donor molecule of the claimed complex is a phthalic acid ester, the



complexed ester molecule is simply formed by replacing the chlorines of the phthalic acid dichloride with alkoxy groups.

According to a first alternative embodiment of the process of the invention, said magnesium compound (a) containing an alkoxy moiety is a magnesium dichloride-magnesium dialkoxide complex of the formula (V):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group, and p is 1 to 6, preferably about 2. Formula (V) is empirical or semiempirical, meaning that the complex's molecular clusters can consist of several MgCl<sub>2</sub> molecules and several Mg(OR')<sub>2</sub> molecules, corresponding to the formula (MgCl<sub>2</sub>)<sub>c</sub>[Mg(OR')<sub>2</sub>]<sub>d</sub> wherein d:c = p. In the process of the invention, said magnesium dichloride-magnesium dialkoxide complex is reacted with the above halogen compound so that the halogen compound (b) has its halogen(s) replaced by the alkoxide(s) of the complex and forms an electron donor, whereby the complex of magnesium dichloride and the electron donor is formed.

Preferably, said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-dimagnesium dialkoxide complex of the structural formula (VI):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

Said magnesium dichloride-magnesium dialkoxide complex is preferably prepared by reacting magnesium dichloride and an alcohol into an intermediate which is a magnesium dichloride-alcohol complex MgCl<sub>2</sub> · (R'OH)<sub>2p</sub> wherein R' is the same as above, and reacting the magnesium dichloride alcohol complex with p mol of a magnesium dialkyl MgR''<sub>2</sub>, wherein R'' is a hydrocarbyl group having 1 to 20 carbon atoms. If R'' is a hydrocarbyl group having 1 to 5 carbon atoms, a volatile alkane R''H byproduct is thereby formed and easily removed by evaporation. In the synthesis, the molar ratio MgCl<sub>2</sub>:R'OH is preferably between 1:1 and 1:8, most preferably between 1:2 and 1:5. The molar ratio MgCl<sub>2</sub> · (R'OH)<sub>2p</sub>:MgR''<sub>2</sub> is preferably between 1:1 and 1:4, most preferably about 1:2.

Said magnesium compound (a) which is said magnesium dichloride-dimagnesium dialkoxide complex  $\text{MgCl}_2 \cdot [\text{Mg}(\text{OR}')_2]_2$ , wherein  $\text{R}'$  is the same as above, is preferably reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene. Typically, the product is

5  $(\text{MgCl}_2)_3 \cdot [\text{Ph}(\text{COOR}')_2]_2$ . See formula (III) above.

In the first alternative embodiment of the claimed process, said magnesium compound (a) and said halogen compound (b) are reacted in essentially stoichiometrical amounts and, independently, at a temperature of between 80 °C and 160 °C. The reaction time is preferably about 2 h to about 8 h.

10 Most preferably, the magnesium dihalide and the alcohol, which is a heavier alcohol, are first reacted at a temperature between 120 °C and 160 °C, after which the product is reacted with the magnesium alkoxide at a temperature between 80 °C and 120 °C, followed by reaction with the halogen compound at said lower temperature interval.

15 A typical example of said first alternative embodiment of the claimed process is described in Figure 1.

According to a second alternative embodiment of the claimed process, said magnesium compound (a) containing an alkoxy moiety is a non-complex magnesium dialkoxide of the formula (VII):



wherein  $\text{R}'$  is a  $\text{C}_1$ - $\text{C}_{20}$  aralkyl group or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl group, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl group.

Said non-complex magnesium dialkoxide is preferably prepared by reacting a magnesium dialkyl, preferably a magnesium dialkyl of the formula  $\text{MgR}''_2$ , wherein

25  $\text{R}''$  is a hydrocarbyl group having 1 to 20 carbon atoms, and an alcohol, preferably an alcohol of the formula  $\text{R}'\text{OH}$ , wherein  $\text{R}'$  is the same as above. The preferred ratio between the magnesium dialkyl and the alcohol is about 1:2.

In the second alternative embodiment of the claimed process, said magnesium compound (a) which is said non-complex magnesium dialkoxide, has the formula

30  $\text{Mg}(\text{OR}')_2$ , wherein  $\text{R}'$  is a  $\text{C}_1$ - $\text{C}_{20}$  aralkyl or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl, is preferably reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene. Usually, said

magnesium compound (a) and said halogen compound (b) are reacted in essentially stoichiometric amounts. The product formed is preferably  $\text{MgCl}_2 \cdot \text{Ph}(\text{COOR}')_2$ . See Formula II above.

5 A typical example of said second alternative embodiment of the claimed process is described in Figure 2.

According to a third alternative embodiment of the process of the invention, said magnesium compound (a) containing an alkoxy moiety is a complex of a magnesium dihalide and an alcohol of the Formula (VIII):



10 wherein R' is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl group, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl group, and q is from 1 and 6. The alkoxy moiety is the R'O group of the alcohol R'OH. This complex is often used as starting material for Ziegler-Natta catalyst components. However, it is not known to have been used as starting material for a magnesium dihalide electron donor complex by reacting it with a  
15 halogenous electron donor precursor in the above described way.

The complex of a magnesium dihalide and an alcohol is usually prepared by reacting magnesium dichloride  $\text{MgCl}_2$  and alcohol R'OH, wherein R' is the same as above.

20 In the process according to the second alternative embodiment, said magnesium compound (a) which is said complex of a magnesium dihalide and an alcohol having the formula  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_q$ , wherein R' is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl, and q is from 1 and 6, is preferably reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene. An example of this third alternative embodiment is described in  
25 Figure 3.

Above, the product and its preparation according to the invention have been described. As the claimed complex finds its natural application in the field of olefin polymerization catalyst synthesis, the invention also relates to the use of said complex in that field. Thus, claimed is the use of said complex for the preparation  
30 of a polymerization catalyst component containing magnesium, as well as at least one transition metal, halogen and electron donor. More specifically, the use is characterized in that said complex is reacted with a titanium halide (c) to give said catalyst component.

Said titanium halide (c) preferably has the Formula (IX):



wherein R''' is a C<sub>1</sub>-C<sub>10</sub> alkyl group or a C<sub>7</sub>-C<sub>16</sub> aralkyl group, X is a halogen and p is 0 to 3. Most preferably, said titanium halide (c) is a titanium tetrahalide TiX<sub>4</sub>,  
5 wherein X is the same as above, most preferably titanium tetrachloride TiCl<sub>4</sub>.

## Experimental

### Preparation of the complexes

All chemicals were handled in strict inert conditions and all the reactions took place also in strict inert conditions in a nitrogen atmosphere.

#### 10 Example 1 (first alternative embodiment)

First 1.07 g (11.2 mmol) of MgCl<sub>2</sub> was introduced into a 50 ml glass reactor. 9.60 ml (8.0 g, 46.2 mmol) of 1-undecanol was added on to the MgCl<sub>2</sub>. The slurry was mixed using a magnetic stirring bar and the solution was heated to 130 °C and the reactants were allowed to react with each other at this temperature for 3 h. The  
15 slurry was cooled down to 100 °C and 9.6 ml (8.3 g, 90 mmol) of toluene was added to the reaction solution to increase its dissolving capability. 25.40 ml (18.52 g, 22.3 mmol R''<sub>2</sub>Mg) of a 20% heptane solution of butyl-octyl magnesium was now introduced. Finally, 3.24 ml (4.565 g, 22.5 mmol) of phthaloyl chloride was added. The achieved product was dried under a stream of nitrogen for several  
20 hours at temperatures between 90 °C and 120 °C.

#### Example 2 (second alternative embodiment)

123.2 mmol of butyl-octyl magnesium was introduced into a 250 ml glass reactor. A 20% heptane solution of the butyl-octyl magnesium containing 2.92 w-% of Mg was used giving a feed volume of 139.4 ml (102.5 g) in the reactor. 244.6 mmol  
25 (38.2 ml, 31.85 g) of 2-ethyl-1-hexanol was then added slowly at room temperature. The addition of alcohol took 23 min. Mixing speed was about 240 rpm. The temperature was increased to 63 °C and the reactants were allowed to react with each other at that temperature for 15 min. After this 122.74 mmol (17.69 ml, 24.92 g) of phthaloyl chloride was added slowly at room temperature. The  
30 temperature was increased during 10 min to 50 °C and the reactants were again allowed to react with each other at that temperature for 5 min. After this the reaction solution was allowed to cool down to room temperature.

28.8 g of the achieved solution was taken into a 100 ml glass reactor for solvent evaporation. The sample was dried under vacuum in a stream of nitrogen gas at 50 °C for 3 h. 12 ml of condensed solvent (heptane) was trapped in the vacuum trap.

5 The product was washed with 60 ml of pentane at 45 °C for 45 min, after which the product was allowed to settle for 45 min and the solid product was separated from the solution. The product was washed a second time with 44 ml of pentane and finally dried under vacuum and in a stream of nitrogen at 50 °C for one hour.

### Example 3 (third alternative embodiment)

10 22.60 mmol (2.15 g) of  $\text{MgCl}_2$  was introduced into a 100 ml glass reactor. To this, 45.19 mmol (7.10 ml, 5.92 g) of 2-ethyl-1-hexanol was added. Finally, 22.60 mmol (3.26 ml, 4.59 g) of phthaloyl dichloride was added to the mixture. The mixture was kept under agitation at 60 °C for 30 min. A solid complex was collected from the vessel by evaporation and washed three times with a 100 ml portion of heptane at 90 °C for 15 min, then with a 100 ml portion of pentane at room temperature and  
15 finally dried. This product was reacted with  $\text{TiCl}_4$  into a catalytically active complex.

### Comparative example

A fourth sample was prepared by introducing 20 mmol  $\text{MgCl}_2$  (1.90 g) in a 150 ml glass reactor equipped with a magnetic stirrer. 20 mmol of di-2-ethyl-hexyl-phthalate (8.0 ml, 7.81 g) (DOP) was then added on to the  $\text{MgCl}_2$ . The reactants  
20 were allowed to react with each other overnight. The product was washed with pentane and dried in the same way as described above.

### Characterization of the products by X-ray diffractometry and Infrared spectroscopy

25 The products were characterized by infrared spectroscopy (IR) and by taking X-ray diffraction patterns of it. The WAXS patterns were collected in reflection mode between 2 and 70° 2  $\theta$  with a Siemens D500 instrument. The diffractometer was equipped with a Cu anode and a graphite monochromator in the reflected beam. The effect used was 40 kV and 35 mA. The  $\text{CuK}\alpha$  radiation wavelength was 1.541 Å.  
30 The sample was loaded in a glove box into a Mylar film covered sample holder.

Di-undecylphthalate (DUP) was used as electron donor reference in the IR studies. The products of examples 1 and 2 were investigated together with the standard DUP. The products of example 1 was analyzed twice: right away and a second time after overnight storage.

- 5 The IR spectra were taken by a Nicolet 510 FTIR equipment with  $2\text{ cm}^{-1}$  resolution. The number of scans were 128. All the samples were investigated as capillary films between two KBr pellets. Pure DUP was not handled in inert conditions, but the  $\text{MgCl}_2$  samples were handled in a glove box in an inert nitrogen environment in order to protect the samples from air and moisture. To get thin enough capillary  
10 films the samples were somewhat heated when placed in between the KBr pellets.

### X-ray characterization

- The X-ray diffraction pattern of the  $\text{MgCl}_2$ -DOP complex is shown in Figure 4. The pattern show no sign of  $\text{MgCl}_2$ . At  $50^\circ 2\Theta$ , where the most significant peak of pure  $\text{MgCl}_2$  is to be found, there is no sign of a peak. This is also the case at  $30^\circ$  and  $35^\circ$   
15  $2\Theta$ . On the other hand, there is a new dominant peak at  $4.5^\circ 2\Theta$  showing that the reflecting layers have been separated far from each other ( $21\text{ \AA}$ ).

- The X-ray diffraction pattern of the product coming from the direct reaction between  $\text{MgCl}_2$  and DOP of the comparative example is shown in Figure 5. The pattern showed that no reaction between these components had occurred, the X-ray  
20 pattern showed pure  $\text{MgCl}_2$  with its significant reflecting signals at  $15^\circ$ ,  $30^\circ$ ,  $35^\circ$  and  $50^\circ 2\Theta$ .

- The results show that in the first three synthesis routes the donor compound had been complexed with  $\text{MgCl}_2$  at a molecular level, thereby breaking up the strong molecular structure of crystalline  $\text{MgCl}_2$  and indicating in situ preparation thereof.  
25 The results show also that in the fourth, direct synthesis route, the donor compound had not been able to form a complex with  $\text{MgCl}_2$  but the product contained only original  $\text{MgCl}_2$ .

### Results by Infrared Spectroscopy

- The samples were prepared and studied by IR spectroscopy according to the  
30 description in the experimental section above. As  $\text{MgCl}_2$  does not have any absorbance spectrum in the IR area from  $4000$  to  $400\text{ cm}^{-1}$ , the IR study concentrated on the changes in the structure of the DOP and DUP complexation to the  $\text{MgCl}_2$ .

The pure DOP and DUP absorbs IR light due to the stretching vibration of the ester carbonyl double bond of the C=O group at the wavelength of  $1729\text{ cm}^{-1}$ . The corresponding stretching vibration of the C-O- bond is to be found at  $1280\text{ cm}^{-1}$  and at  $1100\text{ cm}^{-1}$  (see Figure 6).

- 5 When the  $\text{MgCl}_2$  was co-ordinated to DOP in the molar ratio of 1:1, clear changes in the IR spectrum of DOP could be seen (figure 6, Example 2). The absorption peaks of pure DOP could still clearly be seen which indicates that a part of the carbonyl groups are still unco-ordinated. On the right side of the original C=O absorption peak there is a new shoulder indicating that a part of the C=O groups
- 10 have co-ordinated to Mg causing the double bond of the C=O group to loosen up starting to resemble more a single C-O bond. The proportionally small shift in the position of the "shoulder peak" indicate a weak interaction, i.e. a weak co-ordination of  $\text{MgCl}_2$  to the C=O oxygen. A weak interaction is also indicated by the sign of several secondary "shoulder" peaks.
- 15 When the  $\text{MgCl}_2$  amount was increased by 50% in the complex (Example 1), the proportion of the "shoulder" peak at about  $1690\text{ cm}^{-1}$  increased. There is however no sign of a strong co-ordination (figure 6). The changes in the IR spectra show up even better in the sample that had been stored overnight. Here the main peak of the carbonyl oxygen has shifted from the position of  $1729\text{ cm}^{-1}$  for the pure DUP to
- 20  $1719\text{ cm}^{-1}$ . The results show also that the co-ordinated carboxyl group is influencing the "free" carboxyl group as the position of its peak is shifted  $10\text{ cm}^{-1}$ .

- The same results can be seen in connection with the absorption peak of the C-O-bond. The absorption peak of the C-O- bond in the pure DUP is found at  $1287\text{ cm}^{-1}$ . Looking at the spectra for the  $\text{MgCl}_2\cdot\text{DOP}$  (Example 2) and the  $(\text{MgCl}_2)_{1.5}\cdot\text{DUP}$
- 25 (Example 1) samples there is a corresponding "shoulder" peak forming to the left of the original peak indicating a weak double bond character of the C-O bond. This shift is so strong that the original peak at  $1287^{-1}$  is not any longer detectable in the product that had been stored overnight (figure 6). These results indicate that the Mg in the  $\text{MgCl}_2$  is complexed between the C=O oxygen and the C-O oxygen atoms in
- 30 the  $\text{MgCl}_2\cdot\text{DOP}$  and in the  $\text{MgCl}_2\cdot\text{DUP}$  complex.

- Conclusively it can be said that in the IR spectrum of the pure DUP the peaks show unco-ordinated carbonyl groups, in the  $\text{MgCl}_2\cdot\text{DOP}$  and in the  $\text{MgCl}_2\cdot\text{DUP}$  sample (Example 2) there is a  $\text{MgCl}_2$  co-ordination to one of the carbonyl groups, the other being free, and in the  $(\text{MgCl}_2)_{1.5}\cdot\text{DUP}$  sample (Example 1) there is a partial co-
- 35 ordination of  $\text{MgCl}_2$  to both of the carbonyl groups.

**Examples 4 to 7 (use of the complex according to the first alternative embodiment)**

**Preparation of the catalyst component complex**

5 1.69 g (17.70 mmol) of anhydrous  $\text{MgCl}_2$  was introduced in inert conditions into a 100 ml septum bottle. 11.12 ml (9.27 g, 70.80 mmol) of 2-ethyl-hexanol (EHA) was introduced on to the  $\text{MgCl}_2$  and after this the temperature was increased to 125-128 °C to allow the reaction components to react with each other. After this, 8.81  
10 ml (7.67 g, 83.19 mmol) of toluene was added after the reaction solution had cooled down to 110 °C. After the addition of the toluene the reaction solution was cooled down to 21 °C. Then 40 ml (29.16 g, 35.4 mmol) of a 20 w-% heptane solution of butyl-octyl-magnesium (BOMAG) was added. After this 5.10 ml (7.19 g, 35.4 mmol) of phthaloyl dichloride (PDC) was added to produce a  $\text{MgCl}_2$  donor  
15 complex solution.

**Use of the catalyst component complex**

The  $\text{MgCl}_2$  donor complex according to the first alternative embodiment was now,  
20 drop by drop, added into 38.91 ml (67.16 g, 354 mmol) of  $\text{TiCl}_4$  and allowed to react with this reagent at a temperature of 95 °C. The reactants were allowed to react with each other for 30 min.

After the  $\text{TiCl}_4$  treatment, the complex was allowed to settle and the liquid was  
25 siphoned off. After this, 100 ml (86.6 g, 0.94 mol) of toluene was added on to the complex and the complex was washed in this solution at 90 °C for 20 min. Depending on which of the synthesis was under work, this washing step was done once (Example 1), twice (Example 2), three times (Example 3) or four times (Example 4). Finally, the catalyst complex was washed twice with 65 ml (44.44 g, 0.44 mol)  
30 portions of heptane for 20 min at 80 °C and thereafter, the complex was washed at room temperature with a 55 ml (34.44 g, 0.48 mol) portion of pentane for 20 min to improve the drying conditions. The catalysts were dried under a stream of nitrogen for one hour.

**Chemical characterization of the complexes**

35 The catalyst complexes were characterized with respect to their chemical composition by measuring their Ti and Cl content. The Ti analysis was started by



dissolving the samples in a mixture of nitric and hydrofluoric acid. The metal was measured flame atomic absorption with a nitrous acetylene flame. Chloride was determined after dissolution in dilute sulphuric acid by potentiometric titration with a standard silver nitrate solution.

#### 5 Determination of donors and phthalic anhydride

The determination of the phthalic esters and the phthalic anhydride were done by first dissolving the sample in acetone. The dissolving was improved by keeping the acetone slurry in an ultra-sound bath for 5 min. After this the samples were filtered  
10 and run by solution chromatography. As eluent a solution consisting of water and acetonitrile in the proportion of 4/96 was used. Eluent flow rate was 1.5 ml/min. A photo diode array was used as detector. Each component was identified by comparing the respective retention time and UV spectra with standard components.

#### 15 GC studies to measure alcohol content

To check the conversion rate of the ethanol (EtOH), 2-ethyl-hexanol (EHA), or other alcohol added in the synthesis, the alcohol content of the catalysts were measured by gas chromatography (GC). This was done by first dissolving a 100 mg  
20 sample of the catalyst in 1 ml of n-pentanol. Depending on the alcohol to be measured, an internal alcohol standard was chosen. If ethanol was to be measured the n-pentanol solution contained n-propenol as internal standard. To improve the solubility of the catalyst in the solution, the sample was kept in an ultra-sound bath. To remove the inorganics from the organic solution it was extracted with 1 ml of  
25 water and to ensure full dissolution, another ml of the n-pentanol solution was added. To ensure repeatable equilibrium conditions between the organic layer and the water layer the samples were allowed to stand overnight. The sample for the GC was taken from the alcohol layer. A Hewlett Packard 5890 GC with a 60 m DB-1 column was used for the GC analyses. The column had a diameter of 0.25 mm with  
30 a film thickness of 1  $\mu$ m. An FID detector was used.

#### Bulk polymerization

Propylene was polymerized in stirred tank reactor having a volume of 5 l. About 0.9  
35 ml triethyl aluminium (TEA) as a cocatalyst, ca 0,12 ml of a 100-% solution of cyclohexyl methyl dimethoxy silane as an external donor and 30 ml of n-pentane were mixed and allowed to react for 5 minutes. Half of the mixture was added to the

polymerization reactor and the other half was mixed with ca 20 mg of the catalyst complex. After additional 5 minutes the catalyst/TEA/donor/n-heptane mixture was introduced into the reactor. The Al/Ti mole ratio was 250 and the Al/external donor mol ratio was 10 mol/mol. 70 mmol hydrogen and 1400 g of propylene were introduced into the reactor and the temperature was raised within 15-30 minutes to 70 °C. The polymerization time was 60 minutes, after which the polymer formed was taken out from the reactor. The polymers were characterized with respect to their Melt Flow Rate (MFR<sub>2</sub>), bulk density (BD) and fraction of total solubles in xylene (TS).

## Results

### Preparation of the complexes

The catalyst complexes achieved in this investigation are listed in Table 1.

**Table 1**

The catalyst complexes prepared.

Example	Number of toluene washes	Colour of catalyst	Morphology of catalyst
4	1	Dark wine-red	Freely flowing
5	2	Dark wine-red	Freely flowing
6	3	Dark wine-red	Freely flowing
7	4	Dark wine-red	Freely flowing

### The chemical composition of the catalysts

The chemical composition of the catalysts were measured according to the description in the experimental section. In Table 2 the chemical composition of the catalysts are listed in w-% units, in Table 3 the composition is listed in mol-% units and in Table 4 the molar proportions between Mg, Ti and DOP are compared.

The chemical compositions of the catalysts were as expected on the basis of the reaction equation. With three washes a composition of (MgCl<sub>2</sub>)<sub>6</sub>TiCl<sub>4</sub>DOP was achieved. During the washes, there was a slightly higher wash out of TiCl<sub>4</sub> compared to DOP in the last catalyst. The amount of free alcohol (EHA) was also

very low playing no significant part in the chemical composition (now 0.004-0.006 mol-%), i.e. being about 5% of the mol amount of  $\text{TiCl}_4$  or DOP. The amount of phthalic anhydride was about 50% of the DOP amount. To sum up the results from the chemical measurements it can be said that the chemical composition of the catalyst complex when using the  $\text{MgCl}_2$  enriched  $\text{Mg}(\text{OR}')_2$  as a reagent in the catalyst synthesis is  $(\text{MgCl}_2)_3\text{TiCl}_4\text{DOP}(\text{PA})_{0.5}$ .

**Table 2**

The chemical composition of the catalysts in w-% units

Example	Mg w-%	Ti w-%	DOP w-%	EHA w-%	PA w-%
4	7.8	4.7	33.6	0.72	6.7
5	8.1	4.7	32.0	0.54	7.4
6	10.2	3.2	28.5	0.58	6.5
7	12.9	1.6	21.6	0.51	6.1

**Table 3**

The chemical composition of the catalysts in mol-% units

Example	Mg mol-%	Ti mol-%	DOP mol-%	EHA mol-%	PA mol-%
4	0.321	0.098	0.086	0.0055	0.045
5	0.333	0.098	0.082	0.0041	0.050
6	0.420	0.067	0.073	0.0045	0.044
7	0.531	0.033	0.056	0.0039	0.041

**Table 4**

The molar ratio between Mg, Ti and DOP

Example	Mg	Ti	DOP
4	3.3	1	0.9
5	3.4	1	0.8
6	6.3	1	1.1
7	15.9	1	1.7

### Calculated and found chlorine contents

The chlorine content in the catalysts were calculated on the basis of the Mg and Ti content. The calculations were based on the assumption the Mg was present in the catalyst as  $\text{MgCl}_2$  and Ti as  $\text{TiCl}_4$ . These calculated results were then compared to the measured results. The results are listed in Table 5. The results showed to be in good agreement, which indicates that both Mg and Ti are present in the catalyst complexes in the fully chlorinated form.

#### Table 5

The calculated and the found chlorine content in the catalysts

Example	Calculated Cl w-%	Found Cl w-%
4	36.7	36.9
5	37.6	38.0
6	39.3	39.7
7	42.4	43.8

### Wash out of $\text{TiCl}_4$ -DOP

All the chemical measurements support the same conclusion: due to the toluene,  $\text{TiCl}_4$  and DOP are washed out from the catalyst in a molar proportion of 1:1. This shows up as a constant decrease of the Ti mol-% and the DOP mol-%, and as a constant increase of the Mg mol-% and the Cl mol-%.

### Activity of the catalysts

All the catalyst complexes were test polymerized according to the descriptions in the experimental section. The results are listed in Table 5. The results showed that all the catalyst complexes had about the same activity, being between 1.0 and 1.5 kg PP/g cat.

**Table 6**

The test polymerization results

Example	Activity kg PP/g cat	Activity kg PP/g Ti
4	1.1	23
5	1.2	26
6	1.5	45
7	1.3	81

## 5 MFR of the polymers

In Table 7 the MFR values achieved from the test polymerization results are listed. The results indicated a systematic increase in MFR with increasing number of toluene washes as MFR increases from 2.0 in the first polymer to 13.7 in the third.

10

**Table 7**

The MFR values of the polymers

Example	MFR
4	2.0
5	4.9
6	13.7
7	12.4

## 15 Examples 8 to 13 (use of the complex according to the second alternative embodiment)

### Preparation of the catalyst component complexes

20 All chemicals were handled in strict inert conditions and all the reactions took place also in strict inert conditions in nitrogen atmosphere.

25 8.85 mmol of butyl-octyl-magnesium was introduced into a 150 ml glass reactor. A 20% heptane solution (BOMAG-A) was used giving a feed volume of 10 ml (7.29 g). 17.7 mmol (2.78 ml, 2.32 g) of 2-ethyl-1-hexanol (EHA) was then added at room temperature. The temperature was increased to 60 °C and the reactants were

allowed to react with each other at that temperature for 30 min. After this 8.85 mmol (1.28 ml, 1.80 g) of phthaloyl chloride (PDC) was added and the reactants were again allowed to react with each other for 30 min at 60 °C to give the claimed complex.

5

The resulting solution of the claimed complex was added dropwise into 88.5 mmol (9.73 ml, 16.79 g) of  $\text{TiCl}_4$  that had been preheated to 95 °C. The reactants were also in this case allowed to react with each other for 30 min at 95 °C. After this 60 ml of toluene was added. After the precipitate had settled the mother liquid was  
10 siphoned off. Five different examples were carried out according to this description. After this the catalyst complex was washed with 30 ml portions of toluene. In Example 8, the complex was washed once with toluene, in Example 9 twice, in Example 10 three times, in Example 11 four times and in Example 12 six times with 30 ml portions of toluene. The toluene washes were carried out at 90 °C. Finally,  
15 the complex was washed three times with 30 ml portion of pentane. The complexes were finally dried under a stream of nitrogen. The yield of the catalyst was about 2 g which corresponded to about 75% of the theoretical.

#### Characterization of the catalyst components

20

The catalyst component complexes were analyzed with respect to their Mg, Cl and Ti content. In addition to this, the amount of donor compound, the di-octyl-phthalate (DOP) formed in the synthesis, was measured from the catalysts. To indicate to what degree the formed donor compound (DOP) was decomposing in the synthesis,  
25 the amount of phthalic anhydride (PA) was also measured from the catalysts.

#### IR and X-ray of the unwashed Mg:Ti:DOP complex

A stoichiometric complex of  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DOP}$  was prepared by reacting 6.37 mmol (7.19 ml, 5.24 g) of BOMAG with 12.73 mmol (2.00 ml, 1.67 g) of EHA in a  
30 50 ml glass reactor. After this 6.365 mmol (0.92 ml, 1.29 g) of phthaloyl chloride was introduced and last 6.37 mmol (0.70 ml, 1.21 g) of  $\text{TiCl}_4$  was added. The solid product was washed with pentane and finally, the sample was dried in a stream of nitrogen. The sample was characterized by IR spectroscopy and by means of its X-  
35 ray diffraction pattern.

### The IR studies

IR spectres were taken by means of a Nicolet 510 FTIR equipment with 2 cm<sup>-1</sup> resolution. The number of scans were 128. All the samples were investigated as  
5 capillary films between two KBr tablets. The pure EHA was not handled in inert conditions, while the MgCl<sub>2</sub> samples were handled in a glovebox in an inert nitrogen environment in order to protect the samples from air and moisture.

### X-ray diffraction patterns

10

The WAXS patterns were collected in a reflection mode between 2° and 70° 2 $\theta$  with a Siemens D500 instrument. The diffractometer was equipped with a Cu anode and a graphite monochromator in the reflected beam. The CuK $\alpha$  radiation wave-  
length was 1.541 Å. The effect used was 40 kV and 35 mA. The sample was loaded  
15 in a glovebox into a Mylar film covered sample holder.

### Bulk polymerization

20

The bulk test polymerization was carried out according to the above description relating to the first alternative embodiment.

### Results

#### Preparation of the complexes

The reaction between the Mg-alkyl and the alcohol resulted in a clear solution with  
25 a little bit higher viscosity. The reaction was exothermic as the solution became warm when mixing the reactants, the temperature increase was from room temperature up to 50 °C. When the phthaloyl chloride was added a slight yellow colour appeared. Also this reaction was slightly exothermic. The reaction solution become again freely flowing with a low viscosity.

30 The TiCl<sub>4</sub> was introduced into a 150 ml glass reactor and heated to 95 °C. The Mg solution was then added to the hot TiCl<sub>4</sub> solution dropwise. A beige precipitate started to form right at the beginning of the addition. During addition the solution turned turbid. A partly freely floating precipitate was formed together with more tarlike precipitate that started to foal the reactor walls. To improve the settling  
35 conditions toluene was added to the reaction solution. A satisfactory settling of the product was then achieved so that the reaction solution could be siphoned off.

Depending on the number of toluene washes the resulting product become more freely flowing. If only one toluene wash was used the product was still as agglomerates, but already two toluene washes resulted in a freely flowing powder-like product.

5

In the case of the catalyst components of examples 5, 6 and 7, a joined  $\text{MgCl}_2$ -DOP complex and a joined addition to the  $\text{TiCl}_4$  solution was carried out. After the first toluene wash, 1/3 of the solution slurry was separated. The separated part was then washed with the aliphatic hydrocarbon and dried to give the product of example 5.

10 The remaining part of the slurry was washed a second time with toluene and half of this solution slurry was then taken out from the reactor and undertaken the same hydrocarbon treatment as in Example 5, resulting in the product of Example 6. The remaining part of the catalyst slurry in the reactor was washed twice with toluene and then washed with an aliphatic hydrocarbon in the same way as the first two  
15 examples. This sample was the product of example 7. The catalyst morphologies are listed in Table 8.

**Table 8**

The morphology of the catalysts

20

Example	Number of toluene washes	Morphology of catalyst
8	1	Black agglomerates
9	2	Dark powder
10	4	Dark powder

**The Chemical composition of the catalysts**

25 The Mg, Ti, Cl, DOP, EHA and the phthalic anhydride (PA) content of the catalysts were measured. The results are listed in w-% units in Table 9. In Table 10 the chemical composition is given in mol-% units and in Table 11 the Mg and DOP amounts are compared to the Ti amount on a molar basis. Table 12 shows the Cl content of the catalysts.



**Table 9**

The chemical composition of the catalysts in w-% units

<b>Example</b>	<b>Mg w-%</b>	<b>Ti w-%</b>	<b>DOP w-%</b>	<b>EHA w-%</b>	<b>PA w-%</b>
8	5.7	6.8	47.7	0.26	3.4
9	11.3	3.1	32.2	0.18	2.5
10	13.4	1.4	21.3	0.25	1.7

**Table 10**

The chemical composition of the catalysts in mol-% units

<b>Example</b>	<b>Mg mol-%</b>	<b>Ti mol-%</b>	<b>DOP mol-%</b>	<b>EHA mol-%</b>	<b>PA mol-%</b>
8	0.235	0.142	0.122	0.002	0.023
9	0.465	0.065	0.083	0.001	0.017
10	0.551	0.029	0.055	0.002	0.012

**Table 11**

The molar proportions between Mg and Ti and between DOP and Ti

<b>Example</b>	<b>Mg</b>	<b>Ti</b>	<b>DOP</b>
8	1.7	1	0.86
9	7.2	1	1.28
10	18.9	1	1.87

**Table 12**

The calculated Cl content in the catalysts compared to the measured amounts

<b>Example</b>	<b>Calculated Cl w-%</b>	<b>Found Cl w-%</b>
8	36.8	36.4
9	42.2	45.0
10	43.3	44.5

### Activity of the catalysts

All the catalysts were test polymerized according to the above instructions. The polymerization results are listed in Table 13 in both kg PP/g cat and kg PP/g Ti units. Activities of almost 8 kg PP/g cat were achieved. Catalysis of the Examples 8, 9 and 10 gave good polymerization results, with the highest activity achieved for the catalyst that had been twice washed with toluene. The activities expressed in kg PP/g Ti units showed an linear increase related to the number of toluene washes for the catalysts of Examples 8, 9 and 10. Activities of over 500 kg PP/g Ti were reached.

### Characterization of the polymers

All the polymers were characterized with respect to their melt flow rate (MFR) and bulk density (BD). All the polymers showed to have a MFR<sub>2</sub> between 11-12 g/10 min, indicating a quite good hydrogen response. Bulk densities were between 0.350-0.390 g/ml. The total solubles were between 2 and 3%, being better for the polymers achieved with the catalyst giving higher activity. The results listed in Table 14.

**Table 13**

The polymerization results

Example	Activity kg PP/g cat	Activity kg PP/g Ti
8	2.56	38
9	7.88	254
10	7.33	524

**Table 14**

The polymer properties

Example	MFR 2.16 kg, 10 min	TS %	BD g/ml
8	11.0	3.1	0.360
9	12.37	2.1	0.350
10	11.0	2.1	0.390

### IR studies of the catalyst obtained

IR spectra in the corresponding regions of 1500-1950  $\text{cm}^{-1}$  and of 1000-1450  $\text{cm}^{-1}$  were taken from the resulting catalyst of example 9 and compared to an IR spectrum of a typical active catalyst complex coming from a synthesis starting from a  $\text{MgCl}_2 \cdot (\text{EtOH})_3$  support material. The spectra are essentially different, and also different from the IR spectra of the isolated complexes of  $\text{TiCl}_4/\text{DOP}$  and  $\text{MgCl}_2/\text{DOP}$ .

### X-ray studies of the catalyst obtained

10

As described above, X-ray diffraction patterns were taken from the resulting catalysts and compared to a X-ray pattern from an inactive catalyst complex and a typical active catalyst complex prepared from a  $\text{MgCl}_2 \cdot 3\text{EtOH}$  support material.

15 In the X-ray patterns of  $\text{Mg}(\text{OR})_2$ ,  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DOP}$  produced from  $\text{MgCl}_2 \cdot 3\text{EtOH}$ , and of  $(\text{MgCl}_2)_{1.7} \cdot \text{TiCl}_4 \cdot \text{DOP}$  produced by adding one mol  $\text{MgCl}_2 \cdot \text{DOP}$  to 10 moles of  $\text{TiCl}_4$ , there was a strong peak located between  $5^\circ$  and  $9^\circ 2\theta$ . In addition, there is a halo formation between  $17^\circ$  and  $23^\circ 2\theta$ . The strong peak in the left corner of the pattern indicates that large organic groups are separating metal  
20 layers at a distance of between 9 and 17 Å, the distance depending on the size of the organic compound (DOP or di-undecyl phthalate DUP). It can thus be stated that the X-ray diffraction patterns for the final catalyst complexes originating from the claimed complexes all show unique features originating from the starting compounds of  $\text{Mg}(\text{OR})_2$  and  $\text{MgCl}_2 \cdot \text{DOP}$ . These patterns show almost no sign of  
25 amorphous or crystalline  $\text{MgCl}_2$ .

**Examples 11 (use of the complex according to the second alternative embodiment) and 12 and 13 (use of the complex according to the third alternative embodiment)**

30

The following reagents are used;  $\text{MgCl}_2$  or  $\text{MgR}_2$ , 2-ethyl-hexanol (EHA), phthaloyl dichloride (PDC) and  $\text{TiCl}_4$  and they are added in the molecular proportion of 1:2:1:1. In the first synthesis (Example 11), the Mg-alkyl is reacted with the alcohol, then the phthaloyl chloride (PDC) is added and finally the  $\text{TiCl}_4$  is  
35 added. In the next two syntheses (Examples 12 and 13), the Mg-alkyl is replaced by  $\text{MgCl}_2$ . Either the  $\text{TiCl}_4$  or the phthaloyl chloride is added in the next step, followed by the last reagent. The synthesis set-ups are listed in Table 16.

**Table 16**

Addition order of the reaction components in the catalyst synthesis

Reaction component/Example	11	12	13
MgR <sub>2</sub>	1		
MgCl <sub>2</sub>		1	1
R'OH	2	2	2
PDC	3	3	4
TiCl <sub>4</sub>	4	4	3

5

### Preparation of the complexes

The same volumes of reagents have been used in all the experiments regardless in which order they have been added. Thus 22.22 mmol (25.10 ml, 18.3 g) of a 20% heptane solution of butyl-octyl-Mg (BOMAG) was added in experiments (8) and (9) and 22.60 mmol (2.15 g) of MgCl<sub>2</sub> was added in experiment (10). To this, 45.19 mmol (7.10 ml, 5.92 g) of 2-ethyl-1-hexanol EHA was added. The TiCl<sub>4</sub> mol amount added was equal to the mol amount of MgCl<sub>2</sub> being 22.60 mmol (2.48 ml, 4.29 g) and also equal to the mol amount of PDC added, which was 22.60 mmol (3.26 ml, 4.59 g). The addition orders of the reaction components in each catalyst synthesis are listed in Table 16. All the complexes were washed three times with a 100 ml portion of heptane at 90 °C for 15 min and last with a 100 ml portion of pentane at room temperature. Finally the catalysts were dried under a stream of nitrogen.

20

### Characterization of the catalysts

All the catalysts were characterized with respect to their chemical composition by measuring their Mg, Ti, Cl and di-octyl-phthalate (DOP) content. The Ti and Mg containing catalyst samples were dissolved in a mixture of nitric and hydrofluoric acid and the metals were measured by flame atomic absorption with a nitrous oxide/acetylene flame. Chloride was determined after dissolution in dilute sulphuric acid by potentiometric titration with a standard silver nitrate solution.

The determination of the phthalic esters and the phthalic anhydride were done by first dissolving the sample in acetone. The dissolution was improved by keeping the

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acetone slurry in an ultra-sound bath for 5 min. After this the samples were filtered and run by solution chromatography. As eluent a solution consisting of water and acetonitrile in a proportion of 4/96 was used. The eluent flow rate was 1.5 ml/min. A photo diode array was used as detector. Each component was identified by  
5 comparing its retention time and UV spectra with those of standard components. To further characterize the complexes, IR spectra and X-ray diffraction patterns were taken of them.

### **Bulk polymerization**

10

Propylene was polymerized in a stirred tank reactor having a volume of 5 l. About 0.9 ml triethyl aluminium (TEA) as a cocatalyst, about 0,12 ml of a 100-% solution of cyclohexyl methyl dimethoxy silane as an external donor and 30 ml of n-pentane were mixed and allowed to react for 5 minutes. Half of the mixture was added to the  
15 polymerization reactor and the other half was mixed with ca 20 mg of said catalyst component. After an additional 5 minutes the catalyst/TEA/donor/n-heptane mixture was introduced into the reactor. The Al/Ti mole ratio was 250 and the Al/external donor mol ratio was 10 mol/mol. 70 mmol of hydrogen and 1400 g of propylene were introduced into the reactor and the temperature was raised within 15-30  
20 minutes to 70 °C. The polymerization time was 60 minutes, after which the polymer formed was taken out of the reactor. The polymers were characterized with respect to their Melt Flow Rate (MFR<sub>2</sub>), bulk density (BD) and the fraction of total solubles in xylene (TS).

### **Results**

#### **Chemical composition of the catalysts**

As stated in the experimental section, the catalysts were characterized with respect  
30 to their chemical composition. In Table 17 the chemical composition of the catalysts with respect to the Mg, Ti, di(2-ethyl-1-hexyl)phthalate (DOP), 2-ethyl-1-hexyl alcohol (EHA) and phthalic anhydride PA contents are listed in w-% units and in Table 18 the same species are listed in mol-% units and last, in Table 19 the molar composition between Mg, Ti and DOP are listed. The Examples 11 and 13 are  
35 represented by two catalysts, 11a and 11b, as well as 13a and 13b, respectively. The chlorine contents are listed in Table 20.

**Table 17**

The Mg, Ti, DOP, EHA and PA contents of the catalysts in w-% units

<b>Example</b>	<b>Mg w-%</b>	<b>Ti w-%</b>	<b>DOP w-%</b>	<b>EHA w-%</b>	<b>PA w-%</b>
11a	3.6	5.6	35.6	6.8	4.16
11b	9.9	3.5	34.0	-	-
12	3.9	7.0	35.7	5.3	1.27
13a	4.5	7.0	43.6	5.15	1.6
13b	11.1	3.7	33.0	1.00	0.3

**Table 18**

The Mg, Ti, DOP, EHA and PA contents of the catalysts in mol-% units

<b>Example</b>	<b>Mg mol-%</b>	<b>Ti mol-%</b>	<b>DOP mol-%</b>	<b>EHA mol-%</b>	<b>PA mol-%</b>
11a	0.148	0.117	0.091	0.052	0.028
11b	0.407	0.073	0.087	-	-
12	0.161	0.146	0.091	0.041	0.009
13a	0.185	0.146	0.112	0.040	0.011
13b	0.457	0.077	0.085	0.008	0.002

**Table 19**

Comparison between the molar amounts of Mg, Ti and DOP

<b>Example</b>	<b>Mg/Ti</b>	<b>Ti</b>	<b>DOP/Ti</b>
11a	1.3	1	0.8
11b	5.6	1	1.2
12	1.1	1	0.6
13a	1.3	1	0.8
13b	5.6	1	1.1

**Table 20**

The calculated amounts of Cl in the catalysts compared to the amounts found

Example	Calculated w-%	Found w-%
11a	27.1	26.0
11b	39	-
12	32.1	30.9
13a	33.5	32.4
13b	43.4	44.0

5

**The IR results**

In the IR spectra of the catalyst components of Examples 12 and 13a. There were clear indications of the presence of phthalic anhydride in the catalyst that has been prepared from  $MgR_2$  (Example 11a). The phthalic anhydride was almost totally missing from the samples that had been prepared out of  $MgCl_2$  (Examples 12 and 13a). These results confirm the results of the chemical analysis. The IR spectrum (not shown) for the toluene washed example 10b catalyst showed no traces of phthalic anhydride but to the left of the  $C=O---Ti$  peak a shoulder had appeared indicating the presens of some free carboxylic acid group ( $-COOH$ ).

10  
15**The X-ray diffraction patterns**

The X-ray diffraction patterns for the catalysts show that the addition of  $TiCl_4$  before PDC gives a more crystalline material. Example 12 is still showing the organic separation peak at  $7^\circ 2\theta$  and the halo between  $18^\circ$  and  $22^\circ 2\theta$  but only a slight remain thereof can be seen of the halo in the spectrum of Example 13a. In all patterns there seems to be an additional peak at about  $32^\circ-33^\circ 2\theta$ . This peak is not connected to crystalline  $MgCl_2$ . Some unreacted  $MgCl_2$  seems to be present in the catalyst component of Example 13a which is starting to dominate when the catalyst is washed with toluene.

20  
25

### Polymerization results

All but one (Example 11a) of the catalysts were test polymerized according to the descriptions in the experimental section. The polymerization results both in kg PP/g cat units and in kg PP/g Ti units are listed in Table 21. There was an almost  
 5 logarithmic linear increase in the activities. As a whole it can be said that:

1. Addition of  $\text{TiCl}_4$  before PDC gives better activity (compare Examples 12 and 13).
- 10 2. Starting from  $\text{MgCl}_2$  instead of from  $\text{MgR}_2$  gives higher activity (compare Example 11 with Examples 12 and 13).
3. Toluene wash improves activity (compare Examples 13a and 13b).

**Table 21**

15

The polymerization results

Example	Activity kg PP/g cat.	Activity kg PP/g Ti
11b	0.06	1.3
12	0.4	6.0
13a	1.2	18
13b	2.5	67

### Summary

- 20 In this study a stoichiometric synthesis route was used to produce the  $\text{MgCl}_2\text{-C}_6\text{H}_4(\text{COOR}')_2$  complex.  $\text{MgCl}_2$  and Mg-alkyl have been reacted with an alcohol to form a  $\text{MgCl}_2\text{-Mg-alcoholate}$  complex, a Mg-alcoholate and an  $\text{MgCl}_2\text{-alcohol}$  complex. These Mg-alcoholates or  $\text{MgCl}_2\text{-alcohol}$  complex has then been brought into contact with phthaloyl chloride to give an  $\text{MgCl}_2\text{-donor}$  complex. It was not  
 25 possible to produce an  $\text{MgCl}_2\text{-donor}$  complex of this type through a direct contact between  $\text{MgCl}_2$  and the corresponding donor, which rules out the possibility that this complex could have been formed unintentionally in the prior art. The complex achieved through the synthesis routes described in this study is identifiable through its distinct X-ray diffraction pattern that shows a dominant peak at  $4.5^\circ 2\theta$ . IR  
 30 studies showed that the Mg in the  $\text{MgCl}_2$  is co-ordinated both to the C=O oxygen and the C-O- oxygen in the ester group.



## Claims

1. A complex comprising a magnesium dihalide and an electron donor, **characterized** in that it is a complex of the magnesium dihalide and the electron donor and has the following formula (I) expressing the molar ratio between the magnesium dihalide and the electron donor:



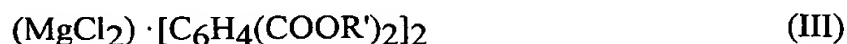
wherein  $\text{MgX}_2$  is the magnesium dihalide and  $\text{R}(\text{OR}')_n$  is the electron donor, X is a halogen, R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, R' is a  $\text{C}_1\text{-C}_{20}$  alkyl group or a  $\text{C}_7\text{-C}_{27}$  aralkyl group, n is a number from 1 to 6 and m is defined as a number  $0.5 \leq m \leq 2.0$ .

2. The complex according to Claim 1, **characterized** in that X is selected from Cl, Br and I, and is preferably Cl.
3. The complex according to Claim 1 or 2, **characterized** in that R is an n-valent  $\text{C}_2\text{-C}_{22}$  acyclic group, preferably an n-valent aromatic  $\text{C}_7\text{-C}_{22}$  acyclic group, most preferably phthaloyl.
4. The complex according to Claim 1, 2 or 3, **characterized** in that R' is a  $\text{C}_6\text{-C}_{16}$  alkyl group, preferably a  $\text{C}_6\text{-C}_{12}$  alkyl group like undecyl or 2-ethyl-1-hexyl.
5. The complex according to any preceding claim, **characterized** in that n is about 1 to about 4, preferably about 2.0.
6. The complex according to any preceding claim, **characterized** in that m is about 0.67 to about 1.0.
7. The complex according to any preceding claim, **characterized** in that it is a magnesium dichloride phthalic acid ester complex having the formula (II):



wherein R' is the same as above.

8. The complex according to one of Claims 1 to 5, **characterized** in that it is a magnesium dichloride phthalic acid ester complex having the formula (III):



wherein R' is the same as above.

9. The complex according to any preceding claim, **characterized** in that it has an X-ray diffraction pattern showing a dominant peak at  $4.5^{\circ}2\Theta$ .

10. Process for the preparation of a complex according to any preceding claim  
 5 comprising a magnesium dihalide and an electron donor, **characterized** by reacting a magnesium compound (a) containing an alkoxy moiety, which magnesium compound is selected from the group consisting of a complex of a magnesium dihalide and a magnesium dialkoxide, a complex of a magnesium dihalide and an alcohol, and a non-complex magnesium dialkoxide, with a halogen compound (b),  
 10 which is capable of forming the electron donor by replacement of its halogen by said alkoxy moiety.

11. Process according to Claim 10, **characterized** in that said halogen compound (b) has the formula (IV):



15 wherein R is an n-valent  $\text{C}_1\text{-C}_{20}$  aliphatic group, an n-valent  $\text{C}_7\text{-C}_{27}$  araliphatic group or an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, X is a halogen and n is 1 to 6.

12. The complex according to Claim 11, **characterized** in that R is an n-valent  $\text{C}_2\text{-C}_{24}$  acyclic group, preferably an n-valent aromatic  $\text{C}_7\text{-C}_{24}$  acyclic group, most preferably phthaloyl.

20 13. Process according to Claim 11 or 12, **characterized** in that X is selected from Cl, Br and I, and is preferably Cl.

14. Process according to Claim 11, 12 or 13, **characterized** in that n is 1 to 4, preferably about 2.

25 15. Process according to any of Claims 11 to 14, **characterized** in that said halogen compound is an organic acid halide, preferably phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene.

16. Process according to any of Claims 10 to 15, **characterized** in that said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-magnesium dialkoxide complex of the formula (V):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group, and p is 1 to 6, preferably about 2.

17. Process according to Claim 16, characterized in that said complex of a magnesium dihalide and a magnesium dialkoxide is a magnesium dichloride-dimagnesium dialkoxide complex of the formula (VI):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> alkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

18. Process according to Claim 16, characterized in that said magnesium dichloride magnesium dialkoxide complex is prepared by reacting magnesium dichloride with and alcohol into an intermediate which is a magnesium dichloride alcohol complex  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_{2p}$ , wherein R' is the same as above, and reacting the magnesium dichloride alcohol complex with p mol of a magnesium dialkyl  $\text{MgR}''_2$ , wherein R'' is a hydrocarbyl group having 1 to 20 carbon atoms.

19. Process according to Claim 18, characterized in that, independently, the molar ratio  $\text{MgCl}_2:\text{R}'\text{OH}$  is between 1:1 and 1:8, preferably between 1:2 and 1:5, the molar ratio  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_{2p}:\text{MgR}''_2$  is between 1:1 and 1:4, preferably about 1:2, the temperature is between 80 °C and 160 °C, and the reaction time is about 2 h to about 8 h.

20. Process according to Claim 15 and 17, characterized in that said magnesium compound (a) which is said magnesium dichloride-dimagnesium dialkoxide complex  $\text{MgCl}_2 \cdot [\text{Mg}(\text{OR}')_2]_2$ , wherein R' is a C<sub>6</sub>-C<sub>16</sub> alkyl group, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein Ph is o-phenylene.

21. Process according to any of Claims 10 to 15, characterized in that said non-complex magnesium dialkoxide has the formula (VIII):



wherein R' is a C<sub>1</sub>-C<sub>20</sub> aralkyl group or a C<sub>7</sub>-C<sub>27</sub> aralkyl group, preferably a C<sub>6</sub>-C<sub>16</sub> alkyl group.

22. Process according to Claim 21, characterized in that said non-complex magnesium dialkoxide is prepared by reacting a magnesium dialkyl, preferably a

magnesium dialkyl of the formula  $\text{MgR}''_2$ , wherein  $\text{R}''$  is a hydrocarbyl group having 1 to 20 carbon atoms, and an alcohol, preferably an alcohol of the formula  $\text{R}'\text{OH}$  wherein  $\text{R}'$  is the same as above.

23. Process according to Claim 15 and 21, characterized in that said magnesium compound (a) which is said non-complex magnesium dialkoxide has the formula  $\text{Mg}(\text{OR}')_2$ , wherein  $\text{R}'$  is a  $\text{C}_1$ - $\text{C}_{20}$  aralkyl or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene.

24. Process according to any of Claims 10 to 15, characterized in that said complex of a magnesium dihalide and a magnesium dialkoxide is a complex of a magnesium dihalide and an alcohol having the formula (VII):



wherein  $\text{R}'$  is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl group, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl group, and  $q$  is from 1 to 6.

25. Process according to Claim 24, characterized in that said complex of a magnesium dihalide and an alcohol is prepared by reacting magnesium dichloride  $\text{MgCl}_2$  and alcohol  $\text{R}'\text{OH}$ , wherein  $\text{R}'$  is the same as above.

26. Process according to Claim 24 or 25, characterized in that the reaction temperature is kept between  $10^\circ\text{C}$  and  $100^\circ\text{C}$ , and the reaction time is about from 10 to about 90 min.

27. Process according to Claim 15 and 24, characterized in that said magnesium compound (a) which is said complex of a magnesium dihalide and an alcohol having the formula  $\text{MgCl}_2 \cdot (\text{R}'\text{OH})_q$ , wherein  $\text{R}'$  is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl or a  $\text{C}_7$ - $\text{C}_{27}$  aralkyl, preferably a  $\text{C}_6$ - $\text{C}_{16}$  alkyl, and  $q$  is from 1 to 6, is reacted with said halogen compound (b) which is said phthalic acid dichloride  $\text{Ph}(\text{COCl})_2$ , wherein  $\text{Ph}$  is o-phenylene.

28. Process according to one of Claims 10 to 27, characterized in that said magnesium compound (a) and said halogen compound (b) are reacted essentially stoichiometrically.

29. Use of a complex according to one of Claims 1 to 9 or a complex prepared according to one of Claims 10 to 28 for the preparation of a polymerization catalyst component containing magnesium, transition metal, halogen and electron donor.

30. Use according to Claim 29, **characterized** in that said complex is reacted with a titanium halide (c).

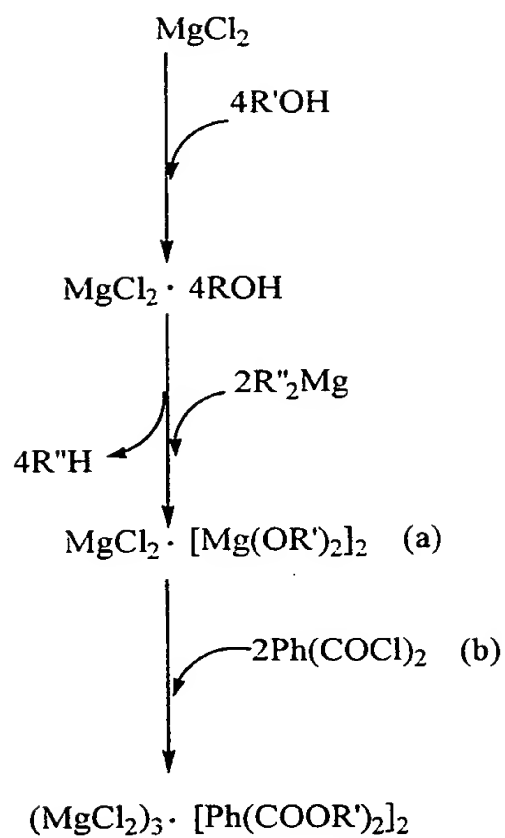
31. Use according to Claim 30, **characterized** in that said titanium halide (c) has the formula (IX):



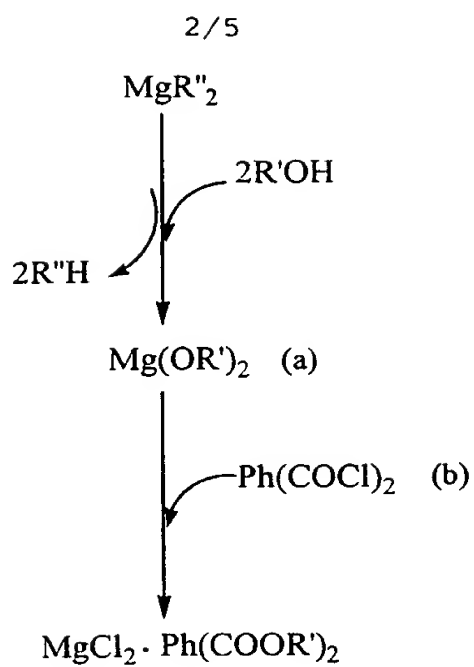
wherein R''' is a C<sub>1</sub>-C<sub>10</sub> alkyl group or a C<sub>7</sub>-C<sub>16</sub> aralkyl group, X is a halogen and p is 0 to 3, and preferably is a titanium tetrahalide TiX<sub>4</sub>, wherein X is the same as above, most preferably titanium tetrachloride TiCl<sub>4</sub>.

10    32. A complex according to one of claims 1 to 9, **characterized** in that it shows an IR spectra with an absorption peak for the C=O...Mg that has shifted 5 to 15 cm<sup>-1</sup>, preferably 10 cm<sup>-1</sup> to the right, and preferably also shows three shoulders.

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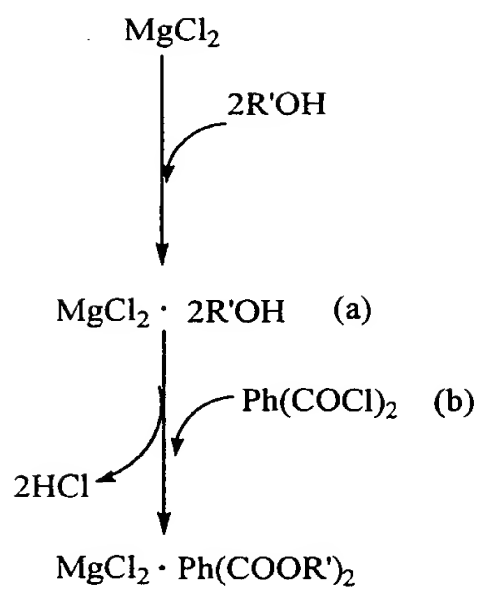


**Figure 1** Example of first alternative embodiment



**Figure 2** Example of second alternative embodiment

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**Figure 3** Example of third alternative embodiment



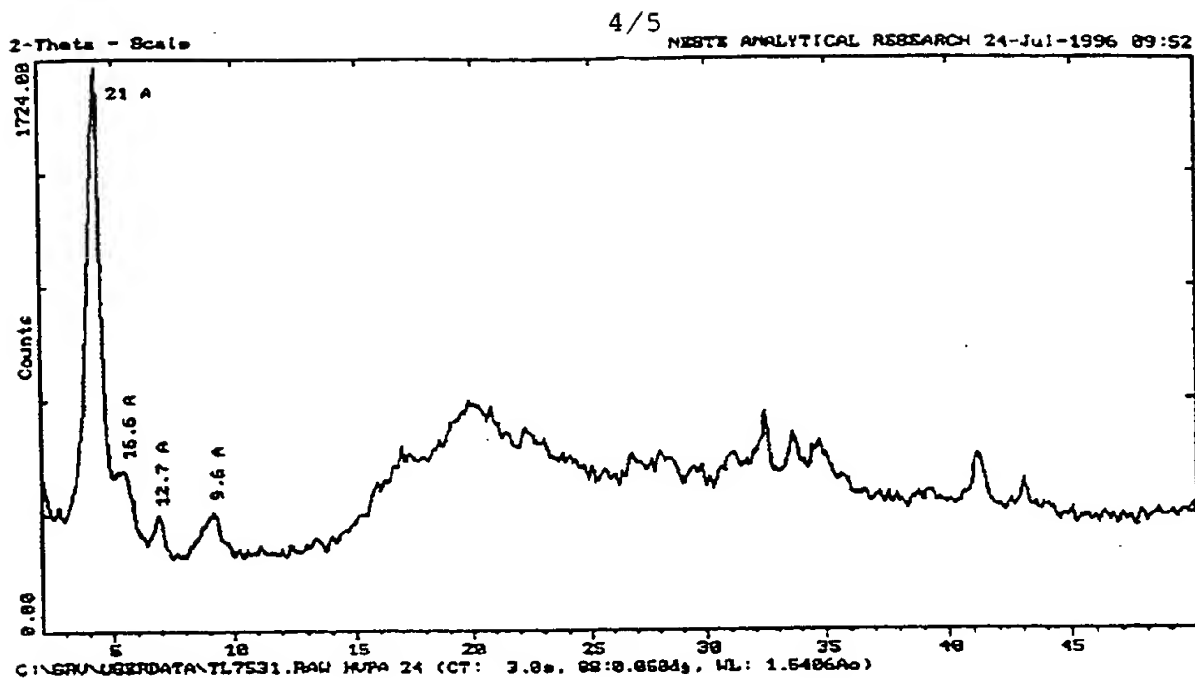


Figure 4 The x-ray diffraction pattern of the Mg-complex produced out of Mg-alkyl, alcohol and phthalic ester (example 2)

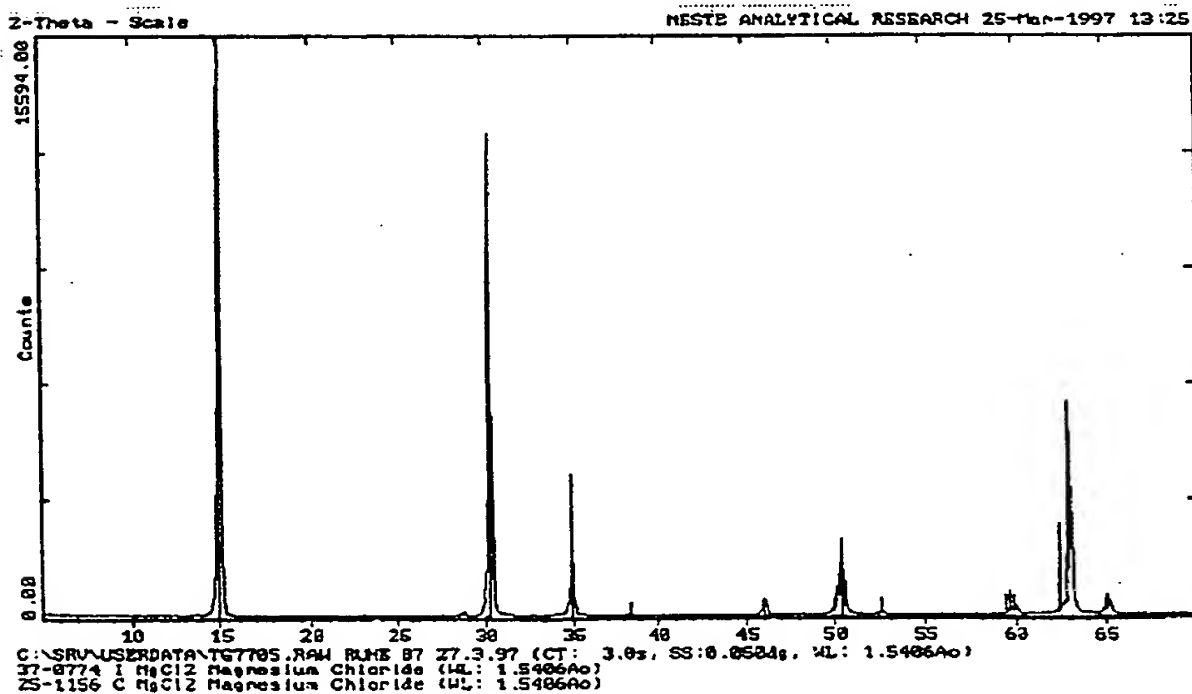
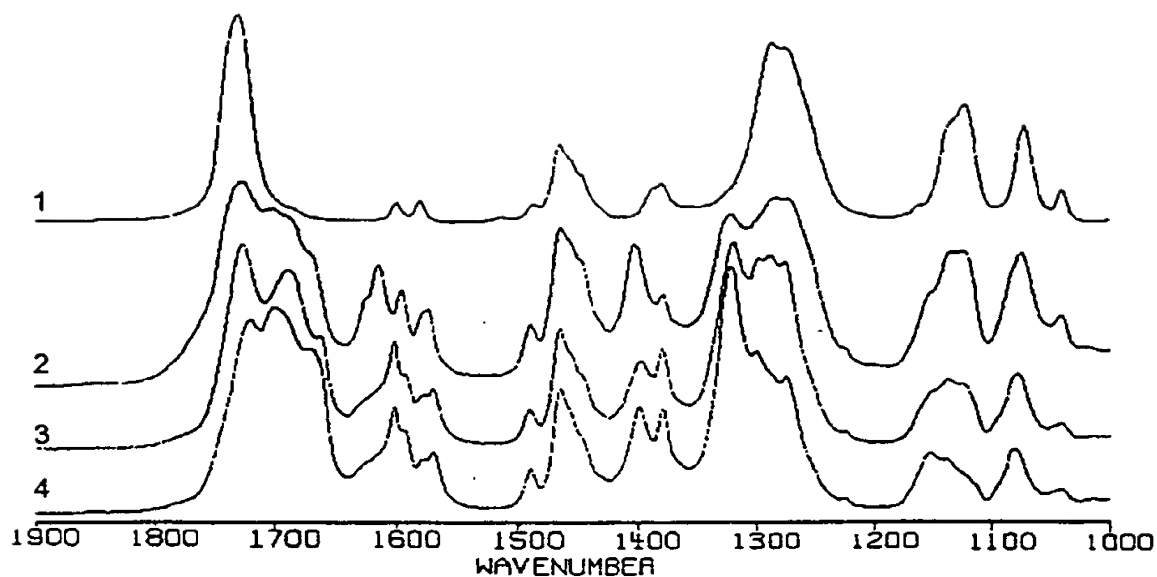


Figure 5 The x-ray diffraction pattern of the product of  $\text{MgCl}_2$  and phthalic ester (comparative example)

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**Figure 6** IR Spectra of  
1 DUP,  
2  $\text{MgCl}_2 \cdot \text{DOP}$  (example 2),  
3  $(\text{MgCl}_2)_{1.5} \cdot \text{DUP}$  (example 1) and  
4  $(\text{MgCl}_2)_{1.5} \cdot \text{DUP}$  (example 1) stored overnight

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/FI 98/01004

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07F3/00 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 297 076 A (LITHIUM CORPORATION OF AMERICA) 28 December 1988 -----	
A	US 4 727 051 A (BREEN, M.J. ET AL.) 23 February 1988 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

7 April 1999

Date of mailing of the international search report

16/04/1999

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Authorized officer

Rinkel, L

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FI 98/01004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			JP 63165388 A	08-07-1988
			PT 86347 B	07-11-1990



## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum)

47134

### Box No. I TITLE OF INVENTION

A soluble magnesium dihalide complex, its preparation and use

### Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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State (that is, country) of residence:  
Denmark

This person is applicant  
for the purposes of:

☐ all designated  
States

☒ all designated States except  
the United States of America

☐ the United States  
of America only

☐ the States indicated in  
the Supplemental Box

### Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

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☒ applicant and inventor

☐ inventor only (If this check-box  
is marked, do not fill in below.)

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State (that is, country) of residence:  
Finland

This person is applicant  
for the purposes of:

☐ all designated  
States

☐ all designated States except  
the United States of America

☒ the United States  
of America only

☐ the States indicated in  
the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

### Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf  
of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

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space above is used instead to indicate a special address to which correspondence should be sent.

## Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

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Massatie 8, FIN-06750 Tolkkinen, Finland

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
Finland

State (that is, country) of residence:  
Finland

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☒ the United States of America only

☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ALA-HUIKKU, Sirpa  
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This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:  
Finland

State (that is, country) of residence:  
Finland

This person is applicant for the purposes of:

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☐ all designated States except the United States of America

☒ the United States of America only

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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

☐ applicant only

☐ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☐ the United States of America only

☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

☐ applicant only

☐ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☐ the United States of America only

☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

## Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

## Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

## National Patent (if other kind of protection or treatment desired, specify on dotted line):

- |  |  |
|--|--|
| <input checked="" type="checkbox"/> AL Albania                               | <input checked="" type="checkbox"/> LS Lesotho                                   |
| <input checked="" type="checkbox"/> AM Armenia                               | <input checked="" type="checkbox"/> LT Lithuania                                 |
| <input checked="" type="checkbox"/> AT Austria                               | <input checked="" type="checkbox"/> LU Luxembourg                                |
| <input checked="" type="checkbox"/> AU Australia                             | <input checked="" type="checkbox"/> LV Latvia                                    |
| <input checked="" type="checkbox"/> AZ Azerbaijan                            | <input checked="" type="checkbox"/> MD Republic of Moldova                       |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina                | <input checked="" type="checkbox"/> MG Madagascar                                |
| <input checked="" type="checkbox"/> BB Barbados                              | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria                              | <input checked="" type="checkbox"/> MN Mongolia                                  |
| <input checked="" type="checkbox"/> BR Brazil                                | <input checked="" type="checkbox"/> MW Malawi                                    |
| <input checked="" type="checkbox"/> BY Belarus                               | <input checked="" type="checkbox"/> MX Mexico                                    |
| <input checked="" type="checkbox"/> CA Canada                                | <input checked="" type="checkbox"/> NO Norway                                    |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein  | <input checked="" type="checkbox"/> NZ New Zealand                               |
| <input checked="" type="checkbox"/> CN China                                 | <input checked="" type="checkbox"/> PL Poland                                    |
| <input checked="" type="checkbox"/> CU Cuba                                  | <input checked="" type="checkbox"/> PT Portugal                                  |
| <input checked="" type="checkbox"/> CZ Czech Republic                        | <input checked="" type="checkbox"/> RO Romania                                   |
| <input checked="" type="checkbox"/> DE Germany                               | <input checked="" type="checkbox"/> RU Russian Federation                        |
| <input checked="" type="checkbox"/> DK Denmark                               | <input checked="" type="checkbox"/> SD Sudan                                     |
| <input checked="" type="checkbox"/> EE Estonia                               | <input checked="" type="checkbox"/> SE Sweden                                    |
| <input checked="" type="checkbox"/> ES Spain                                 | <input checked="" type="checkbox"/> SG Singapore                                 |
| <input checked="" type="checkbox"/> FI Finland                               | <input checked="" type="checkbox"/> SI Slovenia                                  |
| <input checked="" type="checkbox"/> GB United Kingdom                        | <input checked="" type="checkbox"/> SK Slovakia                                  |
| <input checked="" type="checkbox"/> GE Georgia                               | <input checked="" type="checkbox"/> SL Sierra Leone                              |
| <input checked="" type="checkbox"/> GH Ghana                                 | <input checked="" type="checkbox"/> TJ Tajikistan                                |
| <input checked="" type="checkbox"/> GM Gambia                                | <input checked="" type="checkbox"/> TM Turkmenistan                              |
| <input type="checkbox"/> GW Guinea-Bissau                                    | <input checked="" type="checkbox"/> TR Turkey                                    |
| <input checked="" type="checkbox"/> HR Croatia                               | <input checked="" type="checkbox"/> TT Trinidad and Tobago                       |
| <input checked="" type="checkbox"/> HU Hungary                               | <input checked="" type="checkbox"/> UA Ukraine                                   |
| <input checked="" type="checkbox"/> ID Indonesia                             | <input checked="" type="checkbox"/> UG Uganda                                    |
| <input checked="" type="checkbox"/> IL Israel                                | <input checked="" type="checkbox"/> US United States of America                  |
| <input checked="" type="checkbox"/> IS Iceland                               | <input checked="" type="checkbox"/> UZ Uzbekistan                                |
| <input checked="" type="checkbox"/> JP Japan                                 | <input checked="" type="checkbox"/> VN Viet Nam                                  |
| <input checked="" type="checkbox"/> KE Kenya                                 | <input checked="" type="checkbox"/> YU Yugoslavia                                |
| <input checked="" type="checkbox"/> KG Kyrgyzstan                            | <input checked="" type="checkbox"/> ZW Zimbabwe                                  |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea |  |
| <input checked="" type="checkbox"/> KR Republic of Korea                     |  |
| <input checked="" type="checkbox"/> KZ Kazakhstan                            |  |
| <input checked="" type="checkbox"/> LC Saint Lucia                           |  |
| <input checked="" type="checkbox"/> LK Sri Lanka                             |  |
| <input checked="" type="checkbox"/> LR Liberia                               |  |

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- ☒ GD Grenada
- ☒ IN India

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) (23.12.1997) 23 December 1997	974622	Finland (FI)		
item (2) (23.12.1997) 23 December 1997	974623	Finland (FI)		
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): (1) and (2)

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

ISA / EP

**Box No. VIII CHECK LIST; LANGUAGE OF FILING**

This international application contains the following number of sheets:

request : 4  
description (excluding sequence listing part) : 28  
claims : 5  
abstract : 1  
drawings : 5  
sequence listing part of description : \_\_\_\_\_

Total number of sheets : 43

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ other (specify):

Figure of the drawings which should accompany the abstract:

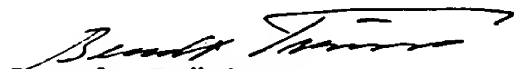
Language of filing of the international application:

English

**Box No. IX SIGNATURE OF APPLICANT OR AGENT**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

BERGGREN OY AB



Berndt Träskman  
Patent Agent  
Helsinki, 21 December 1998

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:



## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>47134</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/FI 98/01004</b>	International filing date (day/month/year) <b>21/12/1998</b>	(Earliest) Priority Date (day/month/year) <b>23/12/1997</b>
Applicant <b>BOREALIS A/S et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**SOLUBLE MAGNESIUM DIHALIDE COMPLEX, PREPARATION AND USE**

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/FI 98/01004

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F3/00 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 297 076 A (LITHIUM CORPORATION OF AMERICA) 28 December 1988 ---	
A	US 4 727 051 A (BREEN, M.J. ET AL.) 23 February 1988 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

7 April 1999

Date of mailing of the international search report

16/04/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/FI 98/01004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 297076	A	28-12-1988	JP 1022882 A	25-01-1989
			US 4820672 A	11-04-1989
<hr/>				
US 4727051	A	23-02-1988	AU 8215487 A	16-06-1988
			CA 1313859 A	23-02-1993
			DE 3785313 A	13-05-1993
			DE 3785313 T	30-09-1993
			EP 0271843 A	22-06-1988
			FI 875351 A	16-06-1988
			JP 63165388 A	08-07-1988
			PT 86347 B	07-11-1990
<hr/>				

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 30 August 1999 (30.08.99)	
International application No. PCT/FI98/01004	Applicant's or agent's file reference 47134
International filing date (day/month/year) 21 December 1998 (21.12.98)	Priority date (day/month/year) 23 December 1997 (23.12.97)
Applicant GAROFF, Thomas et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

13 July 1999 (13.07.99)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer A. Karkachi
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

RECEIVED

BERGGREN OY AB  
P.O. Box 16  
FIN-00101 Helsinki  
FINLANDE

JUN 15 2000

TECH CENTER 1600/2900

Date of mailing (day/month/year) 26 June 2000 (26.06.00)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference 47134	
International application No. PCT/FI98/01004	International filing date (day/month/year) 21 December 1998 (21.12.98)

## 1. The following indications appeared on record concerning:

☒ the applicant    ☐ the inventor    ☐ the agent    ☐ the common representative

Name and Address BOREALIS A/S Lyngby Hovedgade 96 DK-2800 Lyngby Denmark	State of Nationality DK	State of Residence DK
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person    ☒ the name    ☒ the address    ☒ the nationality    ☒ the residence

Name and Address BOREALIS TECHNOLOGY OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

☒ the receiving Office    ☐ the designated Offices concerned  
☐ the International Searching Authority    ☒ the elected Offices concerned  
☐ the International Preliminary Examining Authority    ☐ other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer A. Karkachi Telephone No.: (41-22) 338.83.38
---	---

PATENT COOPERATION TREATY

09/582321

SDFD

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

RECEIVED

BERGGREN OY AB  
P.O. Box 16  
FIN-00101 Helsinki  
FINLANDE

NOV 15 2000

TECH-CENTER 1600/2900

Date of mailing (day/month/year) 26 June 2000 (26.06.00)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference 47134	
International application No. PCT/FI98/01004	International filing date (day/month/year) 21 December 1998 (21.12.98)

## 1. The following indications appeared on record concerning:

☒ the applicant
 ☐ the inventor
 ☐ the agent
 ☐ the common representative

## Name and Address

BOREALIS A/S  
Lyngby Hovedgade 96  
DK-2800 Lyngby  
Denmark

## State of Nationality

DK

## State of Residence

DK

Telephone No.

Facsimile No.

Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person
 ☒ the name
 ☒ the address
 ☒ the nationality
 ☒ the residence

## Name and Address

BOREALIS TECHNOLOGY OY  
P.O. Box 330  
FIN-06101 Porvoo  
Finland

## State of Nationality

FI

## State of Residence

FI

Telephone No.

Facsimile No.

Teleprinter No.

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

☒ the receiving Office
 ☐ the designated Offices concerned  
☐ the International Searching Authority
 ☒ the elected Offices concerned  
☐ the International Preliminary Examining Authority
 ☐ other:
The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

A. Karkachi

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 338.83.38